

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-040652

(43)Date of publication of application : 06.02.2002

(51)Int.Cl.

G03F 7/033  
C08F 2/00  
C08F 2/44  
C08F 2/46  
C08F 4/00  
C08F 20/26  
C08F 20/58  
C08F265/00  
G03F 7/00  
G03F 7/027  
G03F 7/028

(21)Application number : 2000-228902

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(22)Date of filing : 28.07.2000

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## (54) NEGATIVE PHOTSENSITIVE PLANOGRAPHIC PRINTING PLATE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a negative photosensitive planographic printing plate, having high productivity and printing resistance, particularly a negative photosensitive planographic printing plate suitable for pattern forming by laser light.

SOLUTION: The negative photosensitive planographic printing plate is obtained, by disposing on a substrate at least one photosensitive layer containing a polymer binder having at least a repeting structure represented by general formula (I) (where R<sup>1</sup> is H or methyl; R<sup>2</sup> is a (n+1)-valent hydrocarbon group having a 3-30C alicyclic structure; A is O or -NR<sup>3</sup>-; R<sup>3</sup> is H or a 1-10C monovalent hydrocarbon group; and (n) is an integer of 1-5).



## LEGAL STATUS

[Date of request for examination] 01.09.2005

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the negative-mold photosensitivity monotonous printing version suitable for drawing by laser light about the negative-mold photosensitivity monotonous printing version.

[0002]

[Description of the Prior Art] Conventionally, the PS plate which has the configuration which prepared the oleophilic photopolymer layer on the hydrophilic base material as a negative-mold photosensitivity monotonous printing version was used widely, and the desired printing version had usually been obtained as the platemaking approach by carrying out dissolution removal of the non-image section after mask exposure (field exposure) through a lith film. In recent years, the digitization technique which uses a computer, and accumulates [ processes it and ] and outputs image information electronically is spreading widely. And the new image output method corresponding to such a digitization technique has come to be used variously. Computer which manufactures the direct printing version, without scanning according to the image information which had a directive high light like laser light digitized as a result, and minding a lith film Thu It is anxious for the plate (CPT) technique, and it has been an important technical technical problem to obtain the negative-mold photosensitivity monotonous printing version which was adapted for this.

[0003] The configuration which prepared the oleophilic photopolymer layer (henceforth a sensitization layer) containing the photosensitive compound which may generate active species, such as a radical and a bronze TEDDO acid, by laser exposure on the hydrophilic base material as a negative-mold photosensitivity monotonous printing version in which such scan exposure is possible is proposed, and Kamiichi has already been carried out. Based on digital information, carry out the laser scan of this negative-mold photosensitivity monotonous printing version, active species is made to generate, and the lithography version of a negative mold can be obtained by making a sensitization layer carry out lifting insolubilization, and carrying out the development of the physical or chemical change to it succeedingly according to that operation. Especially the negative-mold photosensitivity monotonous printing version that prepared the protective layer of oxygen cutoff nature in the photopolymerization initiator which is excellent in sensitization speed on a hydrophilic base material, the ethylene nature unsaturated compound in which addition polymerization is possible, and the alkali developer the sensitization layer of the photopolymerization mold containing a meltable giant-molecule binder and if needed is excellent in productivity, its development is still simpler, and resolution and impression nature can also serve as the lithographic plate which has the desirable printing engine performance from the advantage of be good.

[0004] Conventionally, the organic giant-molecule polymer in which alkali development, such as the methacrylic-acid copolymer indicated by JP,59-44615,A, JP,54-34327,B, JP,58-12577,B, JP,54-25957,B, JP,54-92723,A, JP,59-53836,A, JP,59-71048,A, etc., an acrylic-acid copolymer, an itaconic-acid copolymer, a crotonic-acid copolymer, a maleic-acid copolymer, and a partial esterification maleic-

acid copolymer, is possible as a giant-molecule binder which constitutes a sensitization layer has been used. However, the negative-mold photosensitivity monotonous printing version which prepared the sensitization layer containing such a conventional giant-molecule binder If scan speed is gathered in order to raise productivity further, since the exposure energy per unit area will become small corresponding to it, Since it had the problem that sufficient hardening is no longer obtained also in the exposure section, the image section received a damage and high print durability was not obtained by the alkali component in a developer, improvement in the further productivity was difficult. Although JP,2000-89460,A has the publication of the positive type photosensitivity monotonous printing version containing a vinyl copolymer including the structural unit which consists of a cyclohexane ring and a carboxyl group, the techniques of this invention differ clearly.

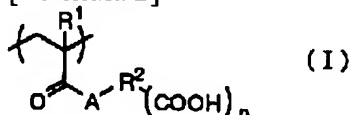
[0005]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the lithography version which conquers the fault of the above-mentioned conventional technique, gives sufficient print durability also in exposure conditions with little exposure energy per unit area, and has high productivity, especially the lithography version suitable for drawing by laser light.

[0006] this invention persons came to accomplish a header and this invention for the above-mentioned purpose being attained by using the acrylic ester which has a carboxyl group and annular aliphatic hydrocarbon structure in coincidence (meta) as a copolymerization component which gives development nature to the giant-molecule binder which constitutes a sensitization layer, as a result of repeating examination wholeheartedly that the above-mentioned purpose should be attained. That is, this invention is the negative-mold photosensitivity monotonous printing version characterized by coming at least to prepare the sensitization layer containing the giant-molecule binder which has the repeat structure expressed with a general formula (I) on a base material further. Here, an acrylic acid (meta) expresses an acrylic acid and/or a methacrylic acid.

[0007]

[Formula 2]



[0008] R1 expresses a hydrogen atom or a methyl group among a general formula (I), and R2 expresses the hydrocarbon group of \*\* which has the aliphatic series cyclic structure of carbon numbers 3-30 (n+1). A expresses an oxygen atom or -NR3-, and R3 expresses a hydrogen atom or the hydrocarbon group of the monovalence of carbon numbers 1-10. n expresses the integer to 1-5.

[0009] One of the descriptions of the negative-mold photosensitivity monotonous printing version of this invention is to use the acrylic ester which has a carboxyl group and annular aliphatic hydrocarbon structure in coincidence (meta) as a copolymerization component which gives alkali development property to a giant-molecule binder. The exposure energy per unit area can give sufficient print durability and high productivity to the negative-mold photosensitivity monotonous printing version of this invention also in few exposure conditions by this. Although originated in exposure energy not being enough for the image section which should be hardened conventionally, the developer permeated, the damage was given to the sensitization layer, although the cause of the effectiveness acquired by this invention was not yet clear, and print durability was reduced By introducing hydrophobic high annular aliphatic hydrocarbon structure near the carboxylic acid, osmosis of the developer in the image section is controlled and it is thought by giving high print durability that it is compatible in productivity and print durability.

[0010]

[Embodiment of the Invention] Hereafter, the sensitization layer of the negative-mold photosensitivity monotonous printing version of this invention is explained to a detail.

The giant-molecule binder which is the description of this invention is explained to the [giant-molecule binder] beginning. the giant-molecule binder (it is also called a binder polymer) used for the

sensitization layer of the negative-mold photosensitivity monotonous printing version in this invention -- carrying out -- the line containing the repeat structure expressed with the above-mentioned general formula (I) -- an organic giant-molecule polymer is used. As a hydrocarbon group of \*\* which has the aliphatic series cyclic structure to the carbon atomic numbers 3-30 as R2 in a general formula (I) (n+1) The cyclopropane which may be permuted more than the piece by the substituent of arbitration, A cyclopentane, a cyclohexane, cycloheptane, cyclooctane, A cyclo decane, dicyclohexyl, TASHI clo hexyl, norbornane, Decahydronaphthalene, a par hydronalium fluorene, tricyclo [5.2.1.02.6] Deccan, Adamantane, a KUADORI cyclane, KONGURESSAN, cubane, spiro [4.4] octane, Cyclopentene, a cyclohexene, a cyclo heptene, cyclooctane, Cyclodecene, cyclohexadiene, cycloheptadiene, cyclo-octadiene, Cycloheptatriene, cyclo deca trien, cyclo-octatriene, NORUBORUNIREN, octahydronaphthalene, bicyclo [2.2.1] heptadiene, Bicyclo [4.3.0] nonadiene, a dicyclopentadiene, a hexahydro anthracene, What made the hydrogen atom on the carbon atom of the arbitration which constitutes the compound which has aliphatic series cyclic structures, such as spiro [4.5] deca diene, the hydrocarbon group of \*\*\*\*\* (n+1) and \*\* (n+1) can be mentioned. R2 is carbon numbers 3-30 including a substituent.

[0011] The carbon atom of the arbitration of the compound which constitutes aliphatic series cyclic structure is a hetero atom chosen from a nitrogen atom, an oxygen atom, or a sulfur atom, and may be replaced more than the piece. As for R2, in respect of print durability, it is desirable that it is the hydrocarbon group of \*\* which has the aliphatic series cyclic structure which may have the substituent to the carbon atomic numbers 5-30 which come to contain two or more rings, such as condensed multi-ring aliphatic hydrocarbon, cross-linking \*\*\*\* aliphatic hydrocarbon, spiro aliphatic hydrocarbon, and an aliphatic hydrocarbon ring set (that with which two or more rings were connected in association or a connection radical), (n+1). Also in this case, a carbon number includes the carbon atom which a substituent has.

[0012] As a substituent, the univalent nonmetal atomic group except hydrogen can be mentioned. A halogen atom (-F, -Br, -Cl, -I), hydroxyl, an alkoxy group, An aryloxy radical, a sulfhydryl group, an alkylthio group, an aryl thio radical, The alkyl dithio, the aryl dithio, the amino group, N-alkylamino radical, The N and N-dialkylamino radical, N-arylamino radical, N, and N-diaryl amino group, An N-alkyl-N-arylamino radical, an acyloxy radical, a carbamoyloxy radical, N-alkyl carbamoyloxy radical, N-aryl carbamoyloxy radical, An N and N-dialkyl carbamoyloxy radical, N, and N-diaryl carbamoyloxy radical, An N-alkyl-N-aryl carbamoyloxy radical, an alkyl sulfoxy radical, An aryl sulfoxy radical, an acyl thio radical, the acylamino radical, N-alkyl acylamino radical, N-aryl acylamino radical, an ureido radical, an N'-alkyl ureido radical, An N' and N'-dialkyl ureido radical, N'-aryl ureide radical, N', and N'-diaryl ureido radical, An N'-alkyl-N'-aryl ureide radical, N-alkyl ureido radical, N-aryl ureide radical, an N'-alkyl-N-alkyl ureido radical, An N'-alkyl-N-aryl ureide radical, N', and N'-dialkyl-N-alkyl ureido radical, An N' and N'-dialkyl-N-aryl ureide radical, an N'-aryl-N-alkyl ureido radical, An N'-aryl-N-aryl ureide radical, N', and N'-diaryl-N-alkyl ureido radical, An N' and N'-diaryl-N-aryl ureide radical, N' - Alkyl-N'-aryl-N-alkyl ureido radical, An N'-alkyl-N'-aryl-N-aryl ureide radical, an alkoxycarbonylamino radical, An aryloxy carbonylamino radical, an N-alkyl-N-alkoxycarbonylamino radical, An N-alkyl-N-aryloxy carbonylamino radical, an N-aryl-N-alkoxycarbonylamino radical, An N-aryl-N-aryloxy carbonylamino radical, a formyl group, An acyl group, a carboxyl group and its conjugate-base radical, an alkoxy carbonyl group, An aryloxy carbonyl group, a carbamoyl group, N-alkyl carbamoyl group, N and N-dialkyl carbamoyl group, N-aryl carbamoyl group, An N and N-diaryl carbamoyl group, an N-alkyl-N-aryl carbamoyl group, An alkyl sulfinyl group, an aryl sulfinyl group, an alkyl sulfonyl group, An aryl sulfonyl group, a sulfonic group (-SO<sub>3</sub>H), and its conjugate-base radical, An alkoxy sulfonyl group, an aryloxy sulfonyl group, a SURUFINA moil radical, N-alkyl SURUFINA moil radical, N, and N-dialkyl SURUFINA moil radical, N-aryl SURUFINA moil radical, a N,N-diarylsulfinamoyl group, An N-alkyl-N-aryl SURUFINA moil radical, a sulfamoyl group, N-alkyl sulfamoyl group, N, and N-dialkyl sulfamoyl group, N-arylsulfamoyl group, an N,N-diaryl sulfamoyl radical, An N-alkyl-N-arylsulfamoyl group, N-acyl sulfamoyl group, and its conjugate-base radical, N-alkyl sulfonyl sulfamoyl group (-SO<sub>2</sub>NHSO<sub>2</sub> (alkyl)) and its conjugate-base radical, N-aryl sulfonyl sulfamoyl group (-

SO<sub>2</sub>NHSO<sub>2</sub> (aryl)) and its conjugate-base radical, N-alkyl sulfonyl carbamoyl group (-CONHSO<sub>2</sub> (alkyl)) and its conjugate-base radical, N-aryl sulfonyl carbamoyl group (-CONHSO<sub>2</sub> (aryl)) and its conjugate-base radical, An alkoxy silyl radical (-Si<sub>3</sub> (Oalkyl)), an aryloxy silyl radical (-Si<sub>3</sub> (Oaryl)), A hydroxy silyl radical (-Si<sub>3</sub> (OH)), the conjugate-base radical and a phosphono radical (-PO<sub>3</sub>H<sub>2</sub>), and its conjugate-base radical, A dialkyl phosphono radical (-PO<sub>3</sub>(alkyl) 2), a diallylphosphono group (-PO<sub>3</sub> (aryl) 2), An alkyl aryl phosphono radical (-PO<sub>3</sub> (alkyl) (aryl)), A monoalkyl phosphono radical (-PO<sub>3</sub>H (alkyl)) and its conjugate-base radical, A mono-aryl phosphono radical (-PO<sub>3</sub>H (aryl)) and its conjugate-base radical, A phosphonooxy radical (-OPO<sub>3</sub>H<sub>2</sub>), and the conjugate-base radical, a dialkyl phosphonooxy radical (-OPO<sub>3</sub>(alkyl) 2), A diaryl phosphonooxy radical (-OPO<sub>3</sub>(aryl) 2), an alkyl aryl phosphonooxy radical (-OPO<sub>3</sub> (alkyl) (aryl)), A monoalkyl phosphonooxy radical (-OPO<sub>3</sub>H (alkyl)) and its conjugate-base radical, A mono-aryl phosphonooxy radical (-OPO<sub>3</sub>H (aryl)) and its conjugate-base radical, A cyano group, a nitro group, a dialkyl BORIRU radical (-B(alkyl) 2), A diaryl BORIRU radical (-B(aryl) 2), an alkyl aryl BORIRU radical (-B (alkyl) (aryl)), A dihydroxy BORIRU radical (-B (OH) 2), the conjugate-base radical and an alkyl hydroxy BORIRU radical (-B (alkyl) (OH)), and its conjugate-base radical, An aryl hydroxy BORIRU radical (-B (aryl) (OH)) and the conjugate-base radical and an aryl group, an alkenyl radical, and an alkynyl group are mentioned.

[0013] Although based also on the design of a sensitization layer, since the substituent which has the hydrogen atom in which hydrogen bond is possible, and especially the substituent that has acidity with an acid dissociation constant (electric dissociation exponent) smaller than a carboxylic acid tend to lower print durability, it is not desirable. On the other hand, since hydrophobic substituents, such as a halogen atom, and a hydrocarbon group (an alkyl group, an aryl group, an alkenyl radical, alkynyl group), an alkoxy group, an aryloxy radical, tend to improve \*\* -proof, they are more desirable, and it is desirable to have such a hydrophobic substituent especially, when cyclic structures are monocycle aliphatic hydrocarbon of six or less membered-rings, such as a cyclopentane and a cyclohexane. If these substituents are possible, it may combine with substituents or the permuted hydrocarbon group, a ring may be formed, and the substituent may be permuted further.

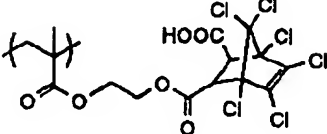
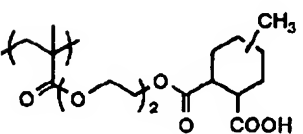
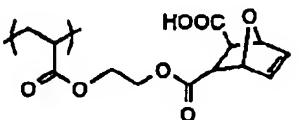
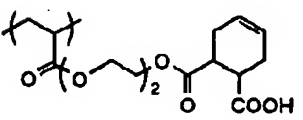
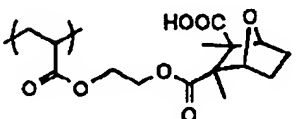
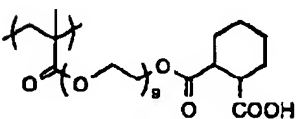
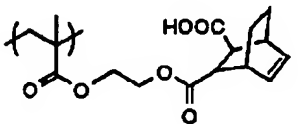
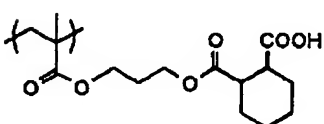
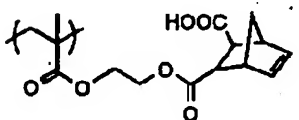
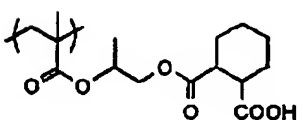
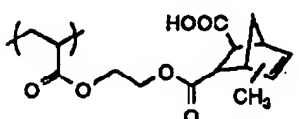
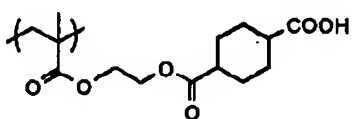
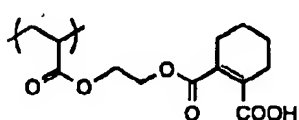
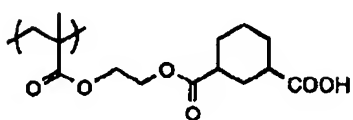
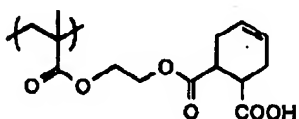
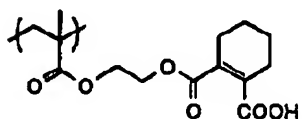
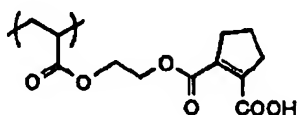
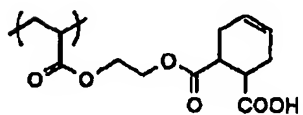
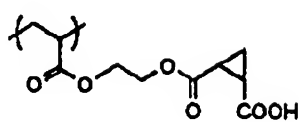
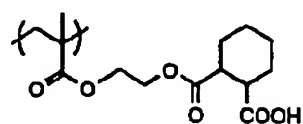
[0014] As a hydrocarbon group of the monovalence to the carbon numbers 1-10 as R<sub>3</sub>, an alkyl group, an aryl group, an alkenyl radical, and an alkynyl group are mentioned. As an example of an alkyl group, a methyl group, an ethyl group, a propyl group, butyl, a pentyl radical and a hexyl group -- passing -- a PUCHIRU radical, an octyl radical, a nonyl radical, and a decyl group -- An isopropyl group, an isobutyl radical, sec-butyl, tert-butyl, An isopentyl radical, a neopentyl radical, 1-methylbutyl radical, an iso hexyl group, The shape of a straight chain to the carbon numbers 1-10, such as a 2-ethylhexyl radical, 2-methyl hexyl group, a cyclopentyl group, a cyclohexyl radical, 1-adamantyl radical, and 2-norbornyl radical, the shape of branching, and an annular alkyl group are mentioned. The hetero aryl group to the carbon numbers 1-10 containing one hetero atom chosen from the group which consists of the aryl group, the nitrogen atom, oxygen atom, and sulfur atom to the carbon numbers 1-10, such as a phenyl group, a naphthyl group, and an indenyl group, as an example of an aryl group, for example, a furil radical, a thienyl group, a pyrrolyl radical, a pyridyl radical, a quinolyl radical, etc. are mentioned. As an example of an alkenyl radical, the shape of a straight chain, the shape of branching, and the annular alkenyl radical to the carbon numbers 1-10, such as a vinyl group, 1-propenyl radical, 1-butenyl group, a 1-methyl-1-propenyl radical, 1-cyclopentenyl radical, and 1-cyclohexenyl group, is mentioned. As an example of an alkynyl group, the alkynyl group to the carbon numbers 1-10, such as an ethynyl group, 1-propynyl radical, 1-butylnyl radical, and 1-OKUCHINIRU radical, is mentioned. It is the same as that of what was mentioned as a substituent which R<sub>2</sub> may have as a substituent which R<sub>3</sub> may have. However, the carbon numbers of R<sub>3</sub> are 1-10 including the carbon number of a substituent.

[0015] Since composition is easy, as for A, it is desirable that they are an oxygen atom or NH. n expresses the integers from 1 to 5. It is 1 preferably in respect of \*\* -proof.

[0016] Although the desirable example of the repeat unit expressed with a general formula (I) below is shown, this invention is not limited to these.

[0017]

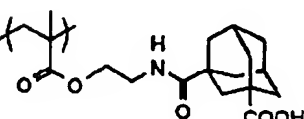
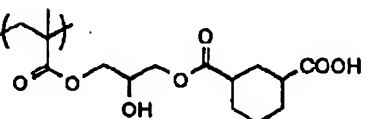
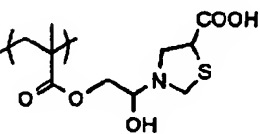
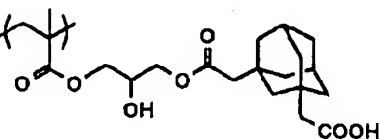
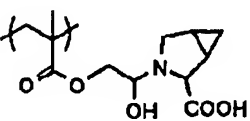
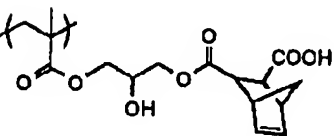
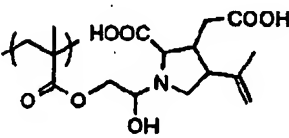
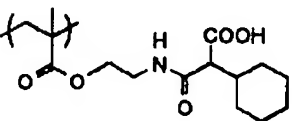
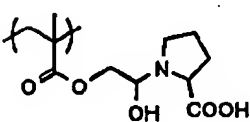
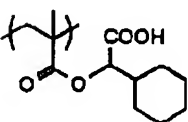
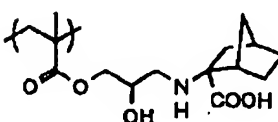
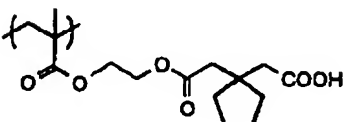
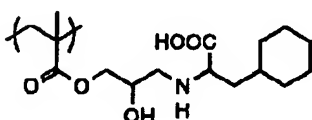
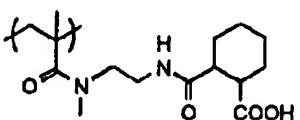
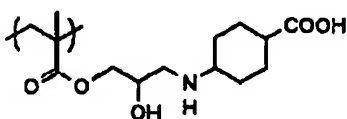
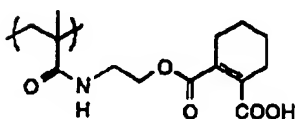
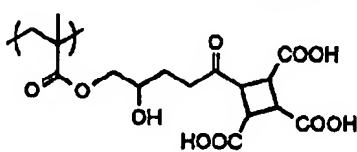
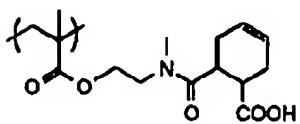
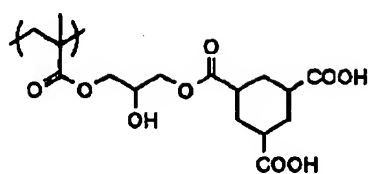
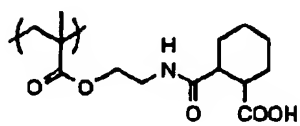
[Formula 3]



[0018]

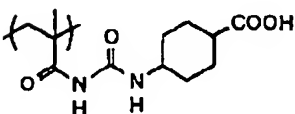
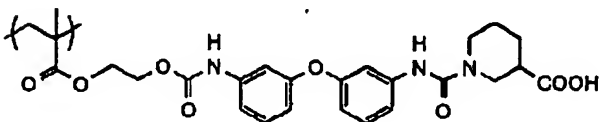
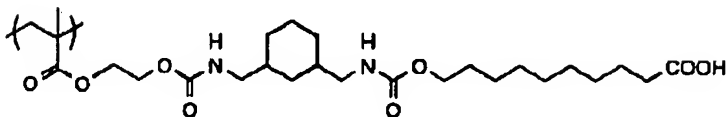
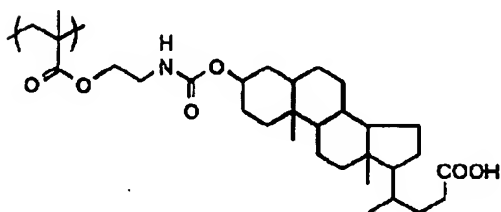
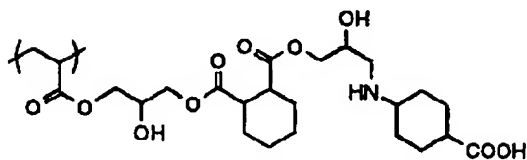
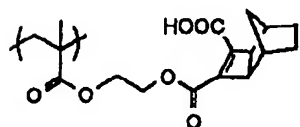
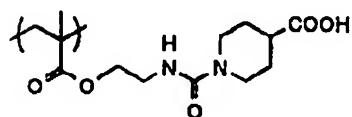
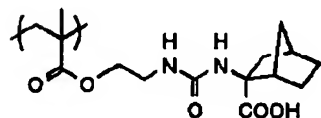
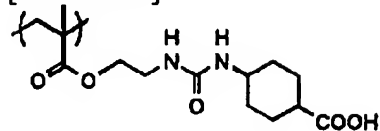
[Formula 4]





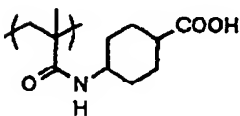
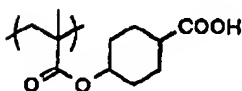
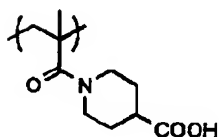
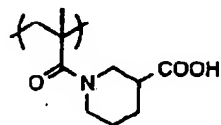
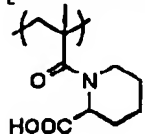
[0019]

[Formula 5]



[0020]

[Formula 6]



[0021] In a binder polymer, the number of the repeat units expressed with a general formula (I) may be one, and they may be contained two or more kinds. Although you may be the polymer which consists only of a repeat unit expressed with a general formula (I), the binder polymer in this invention is combined with other copolymerization components, and is usually used as a copolymer. although the total content of the repeat unit expressed with the general formula (I) in a copolymer is suitably decided by the structure, the design of a sensitization layer, etc. -- desirable -- the total molar quantity of a polymer component -- receiving -- one to 99-mol % -- more -- desirable -- ten to 70-mol % -- it contains in [ 20 to 50 mol ] % still more preferably.

[0022] If it is the monomer in which a radical polymerization is possible as a copolymerization component in the case of using as a copolymer, it can be used that there is no limit of a well-known thing conventionally. Specifically, monomers given in "giant-molecule data handbook-basic volume - (the edited by Society of Polymer Science, Japan, Baifukan, 1986)" are mentioned. The number of such copolymerization components may be one, and they may be used combining two or more kinds.

[0023] The molecular weight of the binder polymer in this invention is suitably determined from a viewpoint of image formation nature or print durability. Usually, although print durability is excellent when molecular weight becomes high, image formation nature tends to deteriorate. On the contrary, print durability becomes low, although image formation nature will become good if low. as desirable molecular weight -- 2,000 to 1,000,000 -- more -- desirable -- 5,000 to 500,000 -- it is the range of 10,000 to 200,000 still more preferably.

[0024] moreover, the giant-molecule binder which has the repeat structure where the giant-molecule binder used for the sensitization layer of the negative-mold photosensitivity monotonous printing version of this invention is expressed with a general formula (I) -- it may be independent, and other giant-molecule binders may be used together one or more sorts, and may be used as mixture. The giant-molecule binder used together is preferably used still more preferably by 1 from 1 in 1 to 20% of the

weight of the range 40% of the weight 60% of the weight to the AUW of a giant-molecule binder component. It can be used that there is no limit of a well-known thing conventionally as a giant-molecule binder which can be used together, and the acrylic principal chain binder which may set in this industry and is specifically used, an urethane binder, etc. are used preferably.

[0025] Although the total quantity of the giant-molecule binder which has the repeat structure expressed with the general formula (I) in the inside of a sensitization layer, and the giant-molecule binder which may be used together can be decided suitably, it is 10 - 90 % of the weight usually 30 - 70% of the weight of the range still more preferably 20 to 80% of the weight preferably to the AUW of the non-volatile component in a sensitization layer.

[0026] Next, the component added in sensitization layers other than a giant-molecule binder is explained. As a negative-mold sensitive material for the image formation used for the sensitization layer of the negative-mold photosensitivity monotonous printing version of this invention, conventionally, if well-known, it can be used without a limit. Although there are combination of light or a heat acid generator, and an acid-catalyst cross-linking compound, combination of the compound which has the ethylene nature unsaturated bond in which light or a thermal polymerization initiator, and radical addition polymerization are possible, etc. as such a negative-mold sensitive material, it is desirable that it is especially the light or the thermal polymerization nature sensitization layer which comes to contain the compound which has light or a thermal polymerization initiator, and the ethylene nature unsaturated bond in which radical addition polymerization is possible. Furthermore, the negative-mold photosensitivity monotonous printing version in this invention is suitable for especially the platemaking in the direct writing in the laser light which has the wavelength of 300 to 1,200nm, and discovers high print durability compared with the conventional lithography version.

[0027] Especially the desirable sensitization layer in the lithography version of [light or thermal polymerization nature negative-mold sensitization layer] this invention is the light or the thermal polymerization nature negative-mold sensitization layer which comes to contain the compound (only henceforth an addition polymerization nature compound) which has the giant-molecule binder and light which have the repeat unit expressed with a general formula (I) as an indispensable component or a thermal polymerization initiator, and the ethylene nature unsaturated bond in which addition polymerization is possible. In addition, various additives, such as a co-sensitizer, a coloring agent, a plasticizer, and polymerization inhibitor, may be added to this sensitization layer if needed.

[0028] The addition polymerization nature compound which is used for [addition polymerization nature compound] light or a thermal polymerization nature negative-mold sensitization layer and which has the ethylene nature partial saturation double bond of a piece at least is chosen from the compound which has preferably at least one end ethylene nature unsaturated bonds [ two or more ]. Such a compound group is widely known in the industrial field concerned, and can use these without limitation especially in this invention. These have the chemical form of a monomer, a prepolymer, i.e., a dimer, a trimer and oligomer or those mixture, those copolymers, etc. As an example of a monomer and its copolymer, unsaturated carboxylic acid (for example, an acrylic acid, a methacrylic acid, an itaconic acid, a crotonic acid, isocrotonic acid, a maleic acid, etc.), and the ester and amides are mentioned, and the ester of unsaturated carboxylic acid and an aliphatic series polyhydric-alcohol compound and the amides of unsaturated carboxylic acid and an aliphatic series multiple-valued amine compound are used preferably. Moreover, a dehydration condensation reaction object with the carboxylic acid of the addition reaction object of the unsaturated-carboxylic-acid ester or the amides which has nucleophilicity substituents, such as hydroxyl, and an amino group, a sulfhydryl group, monofunctional, polyfunctional isocyanates, or epoxy and monofunctional, or many organic functions etc. is used suitably. Moreover, a substitution reaction object with the alcohols of an addition reaction object with the alcohols of the unsaturated-carboxylic-acid ester or the amides which has an isocyanate radical and electrophile nature substituents, such as an epoxy group, monofunctional, or many organic functions, amines, and thiols, the unsaturated-carboxylic-acid ester which has a halogen radical and desorption nature substituents, such as a tosyloxy radical, further or amides, monofunctional, or many organic functions, amines, and thiols is also suitable. Moreover, it is also possible as another example to use the compound group replaced with

partial saturation phosphonic acid, styrene, vinyl ether, etc. instead of the above-mentioned unsaturated carboxylic acid.

[0029] As an example of the monomer of the ester of an aliphatic series polyhydric-alcohol compound and unsaturated carboxylic acid As acrylic ester, ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, Propylene glycol diacrylate, neopentyl glycol diacrylate, Trimethylolpropane triacrylate, the TORIMECHI roll pro pantry (acryloyloxypropyl) ether, Trimethylol triacrylate, hexanediol diacrylate, 1, 4-cyclohexane diol diacrylate, tetraethylene glycol diacrylate, Pentaerythritol diacrylate, a pentaerythritol thoria chestnut rate, Pentaerythritol tetraacrylate, dipentaerythritol diacrylate, Dipentaerythritol hexaacrylate, a sorbitol thoria chestnut rate, There are sorbitol tetraacrylate, sorbitol pentaacrylate, sorbitol hexa acrylate, Tori (acryloyloxyethyl) isocyanurate, polyester acrylate oligomer, etc.

[0030] As methacrylic ester, tetramethylene glycol dimethacrylate, Triethylene glycol dimethacrylate, neopentyl glycol dimethacrylate, Trimethylolpropanetrimethacrylate, trimethylolethane trimethacrylate, Ethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, Hexanedioldimethacrylate, pentaerythritol dimethacrylate, Pentaerythritol trimethacrylate, pentaerythritol tetra-methacrylate, Dipentaerythritol dimethacrylate, dipentaerythritol hexamethacrylate, There are sorbitol trimethacrylate, sorbitol tetra-methacrylate, bis[p-(3-metacryloxy-2-hydroxy propoxy) phenyl] dimethylmethane, screw-[p-(methacrylic oxyethoxy) phenyl] dimethylmethane, etc.

[0031] As itaconic-acid ester, there are ethylene glycol di-itaconate, propylene glycol di-itaconate, 1,3-butanediol di-itaconate, 1,4-butanediol di-itaconate, tetramethylene glycol di-itaconate, pentaerythritol di-itaconate, sorbitol tetra-itaconate, etc. As crotonic-acid ester, there are ethylene GURIKORUJI crotonate, tetramethylene glycol JIKUROTNETO, pentaerythritol JIKUROTNETO, sorbitol TETORAJI crotonate, etc. As isocrotonic acid ester, there are ethylene glycol JIISO crotonate, pentaerythritol JIISO crotonate, sorbitol tetrapod iso crotonate, etc. As a maleate, there are ethylene glycol JIMARETO, triethylene glycol JIMARETO, pentaerythritol JIMARETO, sorbitol tetra-maleate, etc.

[0032] As an example of other ester, JP,46-27926,B, JP,51-47334,B, fatty alcohol system ester given in JP,57-196231,A, JP,59-5240,A, JP,59-5241,A, the thing that has an aromatic series system frame given in JP,2-226149,A, the thing containing the amino group given in JP,1-165613,A, etc. are used suitably. Furthermore, the above-mentioned ester monomer can be used also as mixture.

[0033] Moreover, as an example of the monomer of the amide of an aliphatic series multiple-valued amine compound and unsaturated carboxylic acid, there are methylenebis-acrylamide, methylenebis-methacrylamide, 1, 6-hexa methylenebis-acrylamide, 1, 6-hexa methylenebis-methacrylamide, diethylenetriamine tris acrylamide, xylylene screw acrylamide, xylylene screw methacrylamide, etc. As an example of other desirable amide system monomers, a thing with xylene structure can be raised to cyclo given in JP,54-21726,B.

[0034] The urethane system addition polymerization nature compound manufactured using the addition reaction of isocyanate and a hydroxyl group is also suitable. Moreover, as such an example To for example, the poly isocyanate compound which has two or more isocyanate radicals in one molecule indicated in JP,48-41708,B The vinyl urethane compound containing two or more polymerization nature vinyl groups etc. is mentioned into 1 molecule to which the vinyl monomer containing the hydroxyl group shown by the following general formula (IV) was made to add.

[0035]  $\text{CH}_2=\text{C}(\text{R}_4)\text{COOCH}_2\text{CH}(\text{R}_5)\text{OH}$  (II)

[0036] (However,  $\text{R}_4$  and  $\text{R}_5$  show H or  $\text{CH}_3$ .)

[0037] Moreover, urethane acrylate which is indicated by JP,51-37193,A, JP,2-32293,B, and JP,2-16765,B, and the urethane compounds which have JP,58-49860,B, JP,56-17654,B, JP,62-39417,B, and an ethyleneoxide system frame given in JP,62-39418,B are suitable. Furthermore, the photopolymerization nature constituent which was very excellent in sensitization speed depending on using the addition polymerization nature compounds which is indicated by JP,63-277653,A, JP,63-260909,A, and JP,1-105238,A, and which have amino structure and sulfide structure in intramolecular can be obtained.

[0038] As other examples, acrylate and methacrylate of many organic functions, such as JP,48-64183,A, JP,49-43191,B, JP,52-30490,B, polyester acrylate that are indicated by each official report, and epoxy acrylate the epoxy resin and the acrylic acid (meta) were made to react to, can be mentioned. Moreover, a specific unsaturated compound JP,46-43946,B, JP,1-40337,B, and given in JP,1-40336,B, a vinyl phosphonic acid system compound given in JP,2-25493,A, etc. can be mentioned. Moreover, in a certain case, the structure containing a perfluoro-alkyl group given in JP,61-22048,A is used suitably. Furthermore, it is a Japanese adhesion association magazine. vol.20 and the thing currently introduced to No.7,300-308 page (1984) as a photoresist monomer and oligomer can also be used.

[0039] About these addition polymerization nature compounds, the structure, independent use or concomitant use, and the detail of operation, such as an addition, can be set as arbitration in accordance with the engine-performance design of the final negative-mold photosensitivity monotonous printing version. For example, it is chosen from the following viewpoints. In respect of sensitization speed, structure with many partial saturation radical contents per molecule is desirable, and when it is many, two or more organic functions are desirable. Moreover, in order to make high reinforcement of the image section, i.e., the hardening film, the thing of three or more organic functions is good, and the approach of adjusting both photosensitivity and reinforcement by using together the thing of the different number of organic functions and a different polymerization nature machine (for example, acrylic ester, methacrylic ester, a styrene system compound, a vinyl ether system compound) also has it. [ still more effective ] While the compound of big molecular weight and a hydrophobic high compound are excellent in sensitization speed or film reinforcement, they may not be preferably in respect of a deposit in development speed or a developer. Moreover, also to compatibility with other components in a sensitization layer (for example, a binder polymer, an initiator, a coloring agent, etc.), and dispersibility, selection and the usage of an addition polymerization compound are important factors, for example, may raise compatibility according to use of a low purity compound, and two or more sorts of concomitant use, and it may deal in it. Moreover, specific structure can be chosen for the purpose which makes adhesion, such as a substrate and the below-mentioned overcoat layer, improve. About the compounding ratio of the addition polymerization nature compound in a sensitization layer, although more ones are advantageous in sensibility, when many [ too ], the phase separation which is not preferably arises or problems, like the problem on the production process by the adhesiveness of a sensitization layer (for example, the poor manufacture originating in the imprint of a sensitization layer component and adhesion) and the deposit from a developer arise may be produced. From these viewpoints, an addition polymerization nature compound is preferably used in 25 - 75% of the weight of the range still more preferably five to 80% of the weight to the non-volatile component in a sensitization layer. Moreover, these may be used independently or may be used together two or more sorts. In addition, the usage of an addition polymerization nature compound can choose suitable structure, combination, and an addition as arbitration from viewpoints, such as size of the polymerization inhibition to oxygen, resolution, fogging nature, refractive-index change, and surface adhesiveness, and can also enforce an under coat, and the lamination and the method of application which are called finishing further depending on the case.

[0040] As a [light or thermal polymerization initiator] photopolymerization initiator, the concomitant use system (photopolymerization initiation system) of well-known various photopolymerization initiators or two or more sorts of photopolymerization initiators can be used by a patent, reference, etc. with the wavelength of the light source to be used, choosing it suitably. In making the 2nd higher harmonic of blue semiconductor laser and Ar laser and infrared semiconductor laser, and an SHG-YAG laser into the light source Various photopolymerization initiators (system) are proposed. For example, a photoreduction nature color [ given in U.S. Pat. No. 2,850,445 ] of a certain kind, For example, the system by the combination of colors, such as Lowe's \*\* NGARU, eosine, and erythrosine, or an initiator, For example, the compound initiation system (JP,44-20189,B) of a color and an amine, the concomitant use system of hexaaryl biimidazole, a radical generating agent, and a color (JP,45-37377,B), the system (JP,47-2528,B --) of hexaaryl biimidazole and p-dialkylamino benzylidene ketone JP,54-155292,A, the system of an annular cis--alpha-dicarbonyl compound and a color (JP,48-84183,A),

The system of annular triazine and merocyanine coloring matter (JP,54-151024,A), The system of a 3-keto coumarin and an activator (JP,52-112681,A, JP,58-15503,A), Biimidazole, a styrene derivative, the system of a thiol (JP,59-140203,A), the system (JP,59-1504,A and JP,59-140203,A --) of organic peroxide and coloring matter JP,59-189340,A, JP,62-174203,A, JP,62-1641,B, the system (JP,63-1718105,A --) of U.S. Pat. No. 4766055, a color, and an activity halogenated compound the system (JP,62-143044,A --) of colors, such as JP,63-258903,A and Japanese Patent Application No. No. 63054 [ two to ], and a borate compound JP,62-150242,A, JP,64-13140,A, JP,64-13141,A, JP,64-13142,A, JP,64-13143,A, JP,64-13144,A, JP,64-17048,A, JP,1-229003,A, JP,1-298348,A, the system (JP,2-179643,A --) of the coloring matter and the radical generating agent which have rhodanine rings, such as JP,1-138204,A JP,2-244050,A, the system of titanocene and 3-keto coumarin coloring matter (JP,63-221110,A), the system (JP,4-221958,A --) which combined the ethylene nature unsaturated compound which contains the amino group or a urethane group in titanocene and a xanthene coloring matter pan, and in which addition polymerization is possible The system (JP,8-334897,A) of coloring matter which has JP,4-219756,A, titanocene, the system (JP,6-295061,A) of specific merocyanine coloring matter and titanocene, and a benzopyran ring can be mentioned.

[0041] In the sensitization layer of the negative-mold photosensitivity monotonous printing version of this invention, especially a desirable photopolymerization initiator (system) contains at least one sort of titanocene. When an optical exposure is carried out under coexistence with other sensitizing dye, as long as the titanocene compound used as a photopolymerization nature initiator (system) in this invention is a titanocene compound which may generate an activity radical, it may be any, for example, it can choose suitably the well-known compound indicated by JP,59-152396,A, JP,61-151197,A, JP,63-41483,A, JP,63-41484,A, JP,2-249,A, JP,2-291,A, JP,3-27393,A, JP,3-12403,A, and JP,6-41170,A, and it can be used for it.

[0042] Still more specifically G cyclopentadienyl-Ti-G chloride, G cyclopentadienyl-Ti-screw-phenyl, G cyclopentadienyl-Ti-screw - 2, 3, 4, 5, 6-pentafluoro FENI-1-IRU ("T-1" is said below.) G cyclopentadienyl-Ti-screw - 2, 3, 5, 6-tetrafluoro FENI-1-IRU, G cyclopentadienyl-Ti-screw - 2, 4, 6-trifluoro FENI-1-IRU, The G cyclopentadienyl-Ti-screw -2, 6-difluoro FUENI-1-IRU, The G cyclopentadienyl-Ti-screw -2, 4-difluoro FUENI-1-IRU, G methylcyclopentadienyl-Ti-screw - 2, 3, 4, 5, 6-pentafluoro FUENI-1-IRU, G methylcyclopentadienyl-Ti-screw - 2, 3, 5, 6-tetrafluoro FUENI-1-IRU, The G methylcyclopentadienyl-Ti-screw -2, 4-difluoro FUENI-1-IRU, bis(cyclopentadienyl)-bis(2, 6-difluoro-3-(pill-1-IRU) phenyl) titanium ("T-2" is said below.) etc. -- it can mention.

[0043] These titanocene compounds can also perform various chemical modification for improving the property of a sensitization layer further. For example, approaches, such as substituent installation for association with sensitizing dye and the radical generating PERT of an addition polymerization nature unsaturated compound and others, installation of a hydrophilic part, the improvement in compatibility, and crystal deposit control, substituent installation which raises adhesion, and polymer-izing, can be used. It can be suitably set as arbitration by the engine-performance design of the negative-mold photosensitivity monotonous printing version like the addition polymerization nature compound of point \*\* also about the usage of these titanocene compounds. For example, the compatibility to a sensitization layer can be raised by using two or more sorts together. More [ usually ] ones of the amount of the photopolymerization initiators used, such as the above-mentioned titanocene compound, are advantageous in respect of photosensitivity, and 0.5 - 80 weight sections, and photosensitivity sufficient by using in the range of 1 - 50 weight section preferably are acquired to the non-volatile component 100 weight section of a sensitization layer. On the other hand, sufficient photosensitivity can be acquired even if it lowers the amount of the titanocene used to a pan below the 1.9 weight section below 6 weight sections with combination with other sensitizing dye at a pan below at the 1.4 weight section on the occasion of use by the formation of a whites LGT, such as yellow which is the main purposes of this invention, although few things of the amount of the point of the fogging nature by the light near 500nm to the titanocene used are desirable.

[0044] When making into the light source laser which emits 760 to 1,200nm infrared radiation, it is usually indispensable to use an infrared absorption agent. The infrared absorption agent has the function

to change the absorbed infrared radiation into heat. Under the present circumstances, with the generated heat, a radical generating agent pyrolyzes and a radical is generated. The infrared absorption agent used in this invention is the color or pigment which has the absorption maximum in 1200nm from the wavelength of 760nm.

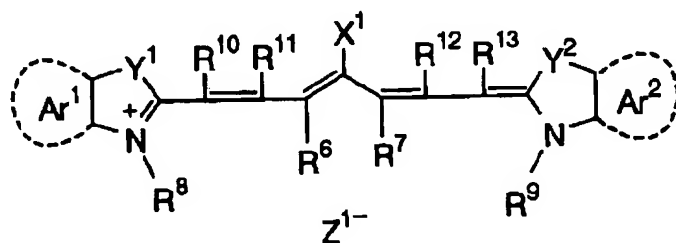
[0045] As a color, the well-known thing indicated by reference, such as a commercial color and a "color handbook" (the Society of Synthetic Organic Chemistry, Japan edit, Showa 45 annual publications), can be used. Specifically, colors, such as azo dye, metallic complex azo dye, pyrazolone azo dye, a naphthoquinone color, anthraquinone dye, phthalocyanine dye, a carbonium color, a quinonimine dye, methine dye, cyanine dye, SUKUWARIRIUMU coloring matter, pyrylium salt, and a metal thio rate complex, are mentioned. As a desirable color, for example JP,58-125246,A, JP,59-84356,A, The cyanine dye indicated by JP,59-202829,A, JP,60-78787,A, etc., The methine dye indicated by JP,58-173696,A, JP,58-181690,A, JP,58-194595,A, etc., JP,58-112793,A, JP,58-224793,A, JP,59-48187,A, The naphthoquinone color indicated by JP,59-73996,A, JP,60-52940,A, JP,60-63744,A, etc., Cyanine dye the SUKUWARIRIUMU coloring matter indicated by JP,58-112792,A etc. and given in British JP,434,875,B etc. can be mentioned.

[0046] Moreover, a near-infrared absorption sensitizer given in U.S. Pat. No. 5,156,938 is also used suitably. Moreover, the arylbenzo(thio)pyrylium salt by which the U.S. Pat. No. 3,881,924 publication was permuted, TORIMECHIN thia pyrylium salt given in JP,57-142645,A (U.S. Pat. No. 4,327,169), JP,58-181051,A, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063, The pyrylium system compound indicated by 59-146061, cyanine dye given in JP,59-216146,A, The pyrylium compound currently indicated by the pentamethine thio pyrylium salt of a publication, etc. JP,5-13514,B, and 5-19702 is also preferably used for U.S. Pat. No. 4,283,475. moreover, the near-infrared absorption color which is indicated by the formula (I) as another example desirable as a color, and is indicated by the U.S. Pat. No. 4,756,993 detail in the letter as (II) can be mentioned. As a desirable thing, cyanine dye, SUKUWARIRIUMU coloring matter, pyrylium salt, and a nickel thio rate complex are especially mentioned among these colors. Furthermore, cyanine dye is desirable and the cyanine dye shown especially by the following general formula (III) is the most desirable.

[0047]

[Formula 7]

一般式 (III)



[0048] X1 shows a halogen atom or X2-L1 among a general formula (III). Here, X2 shows an oxygen atom or a sulfur atom, and L1 shows the hydrocarbon group of the carbon atomic numbers 1-12. R6 and R7 show the hydrocarbon group of the carbon atomic numbers 1-12 independently, respectively. Especially the thing for which it is desirable that it is the hydrocarbon group of two or more carbon atomic numbers as for R6 and R7, R6 and R7 are mutually combined further from the preservation stability of sensitization layer coating liquid, and five membered-rings or six membered-rings are formed is desirable.

[0049] even if Ar1 and Ar2 are the same respectively, they may differ from each other, and they show the aromatic hydrocarbon radical which may have the substituent. The benzene ring and a naphthalene ring are mentioned as a desirable aromatic hydrocarbon radical. Moreover, as a desirable substituent, the alkoxy group of the hydrocarbon group of 12 or less carbon atomic numbers, a halogen atom, and 12 or less carbon atomic numbers is mentioned. even if Y1 and Y2 are the same respectively, they may differ from each other, and they show the dialkyl methylene group of a sulfur atom or 12 or less carbon atomic

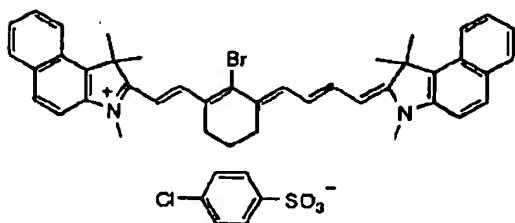
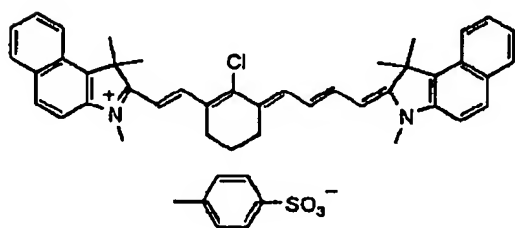
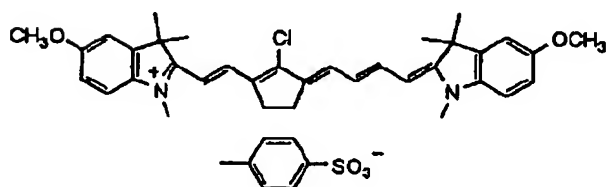
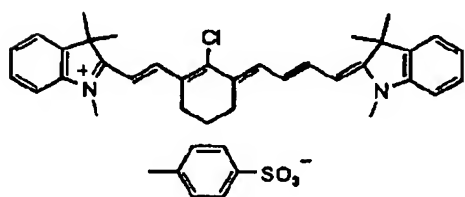
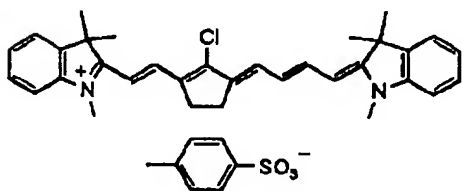
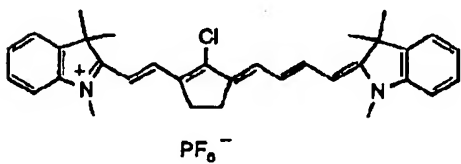
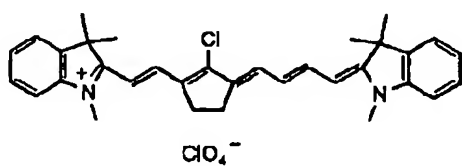


numbers. even if R8 and R9 are the same respectively, they may differ from each other, and they show the hydrocarbon group of 20 or less carbon atomic numbers which may have the substituent. As a desirable substituent, the alkoxy group of 12 or less carbon atomic numbers, a carboxyl group, and a sulfonic group are mentioned. even if R10, R11, R12, and R13 are the same respectively, they may differ from each other, and they show a hydrogen atom or the hydrocarbon group of 12 or less carbon atomic numbers. From the availability of a raw material, it is a hydrogen atom preferably. Moreover, Z1- shows an opposite anion. However, Z1- is unnecessary when the sulfonic group is permuted by either of R6 to R13. Desirable Z1- is the halogen ion from preservation stability, the perchloric acid ion, the tetrafluoroborate ion, hexafluorophosphate ion, and sulfonic-acid ion of sensitization layer coating liquid, and is perchloric acid ion, hexafluoro phosphate ion, and aryl sulfonic-acid ion especially preferably.

[0050] In this invention, what was indicated by the following Japanese-Patent-Application-No. No. 310623 [ 11 to ] specifications can be mentioned as an example of the cyanine dye shown by the general formula (III) which can be used suitably.

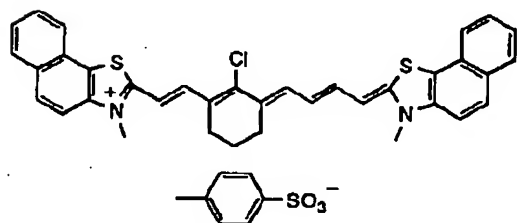
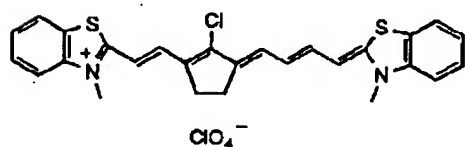
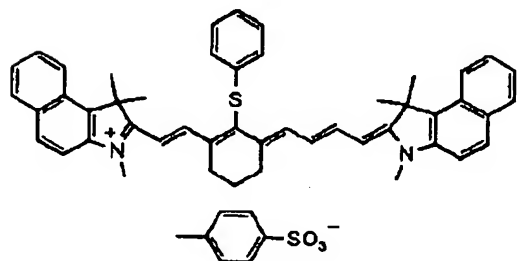
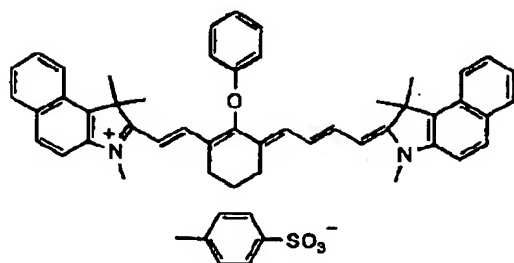
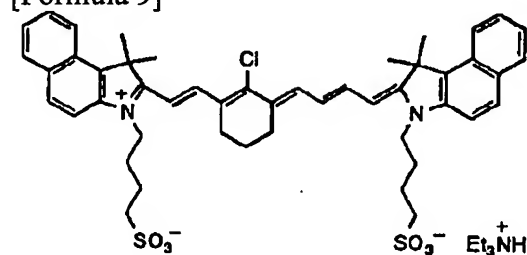
[0051]

[Formula 8]



[0052]

[Formula 9]



[0053] As a pigment used in this invention, the pigment indicated by a commercial pigment and a Color Index (C. I.) handbook, the "newest pigment handbook" (volume for Japanese pigment American Institute of Technology, 1977 annual publications), the "newest pigment applied technology" (CMC publication, 1986 annual publications), "printing ink technical" CMC publication, and 1984 annual publications can be used. As a class of pigment, a black pigment, a yellow pigment, an orange pigment, brown pigments, red pigments, a purple pigment, a blue pigment, green pigments, a fluorescent pigment, a metallic flake pigment, and other polymer joint coloring matter are mentioned. Specifically, insoluble azo pigment, an azo lake pigment, a disazo condensation pigment, a chelate azo pigment, phthalocyanine pigment, an anthraquinone system pigment, perylene and a peri non system pigment, a

thioindigo system pigment, the Quinacridone system pigment, a dioxazine system pigment; an isoindolinone system pigment, a kino FUTARON system pigment, a blue-and-white porcelain lake pigment, an azine pigment, a nitroso pigment, a nitro pigment, a natural pigment, a fluorescent pigment, an inorganic pigment, carbon black, etc. can be used. A desirable thing is carbon black among these pigments.

[0054] These pigments may be used without carrying out surface treatment, may perform surface treatment and may be used. In the approach of surface treatment, the approach of carrying out the surface coat of resin or the wax, the approach to which a surfactant is made to adhere, the method of combining the active substance (for example, a silane coupling agent, an epoxy compound, poly isocyanate, etc.) with a pigment front face, etc. can be considered. The above-mentioned surface treatment approach is indicated by "the property of metallic soap, application" (Saiwai Shobo), the "printing ink technique" (CMC publication, 1984 annual publications), and the "newest pigment applied technology" (CMC publication, 1986 annual publications). As for the particle size of a pigment, it is desirable that it is in the range of 0.01 to 10 micrometers, it is still more desirable that it is in the range of 0.05 to 1 micrometer, and it is desirable that it is in the range of 0.1 to 1 micrometer especially. When the particle size of a pigment is less than 0.01 micrometers, it is not desirable in respect of the stability in the inside of the image sensitization layer coating liquid of a distributed object, and if 10 micrometers is exceeded, it is not desirable in respect of the homogeneity of an image sensitization layer. As an approach of distributing a pigment, the well-known distributed technique used for ink manufacture, toner manufacture, etc. can be used. As a disperser, an ultrasonic distribution machine, a sand mill, attritor, a pearl mill, a super mill, a ball mill, an impeller, DESUPAZA, KD mill, a colloid mill, a dynatron, 3 roll mills, a pressurized kneader, etc. are mentioned. For details, it is indicated by the "newest pigment applied technology" (CMC publication, 1986 annual publications).

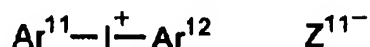
[0055] Although you may add in a sensitization layer, and another layer, for example, finishing coat, and an under coat may be prepared and you may add there, when these infrared absorption agents create the negative-mold photosensitivity lithography version, it is desirable that the optical density in the absorption maximum in the range of 1200nm is from 0.1 to 3.0 from the wavelength of 760nm of a sensitization layer. When it separates from this range, there is an inclination for sensibility to become low. Since optical density is determined by the addition of said infrared absorption agent, and the thickness of a sensitization layer, predetermined optical density is obtained by controlling both conditions. The optical density of a sensitization layer can be measured with a conventional method. As a measuring method, the sensitization layer of the thickness by which the coverage after desiccation was suitably determined in the range required as a lithography version on transparency or a white base material is formed, a sensitization layer is formed on the base material of reflexivity, such as the approach of measuring with the optical-density plan of a transparency mold, and aluminum, and the approach of measuring reflection density etc. is mentioned, for example.

[0056] A pyrolysis mold radical generating agent is used combining said infrared absorption agent, and when it irradiates infrared laser, it points out the compound which generates a radical. Although the triazine compound which has onium salt and a trihalomethyl group, a peroxide, an azo system polymerization initiator, an azide compound, quinone diazide, etc. are mentioned as a radical generating agent, onium salt is high sensitivity and desirable. The onium salt which can be suitably used as a radical polymerization initiator in this invention is explained. As desirable onium salt, iodonium salt, diazonium salt, and sulfonium salt are mentioned. In this invention, these onium salt functions not as an acid generator but as an initiator of a radical polymerization. The onium salt suitably used in this invention is onium salt expressed with (VI) from the following general formula (IV).

[0057]

[Formula 10]

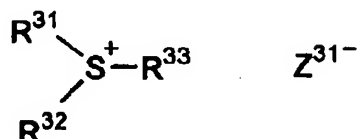
## 一般式 (IV)



## 一般式 (V)



## 一般式 (VI)



[0058] Ar11 and Ar12 show independently the aryl group of 20 or less (the carbon number of a substituent is included) carbon atomic numbers which may have the substituent among a formula (IV), respectively. As a desirable substituent in case this aryl group has a substituent, a halogen atom, a nitro group, the alkyl group of 12 or less carbon atomic numbers, the alkoxy group of 12 or less carbon atomic numbers, or the aryloxy group of 12 or less carbon atomic numbers is mentioned. Z11- expresses halogen ion, perchloric acid ion, tetrafluoroborate ion, hexafluorophosphate ion, and the counter ion chosen from the group which consists of sulfonic-acid ion, and is perchloric acid ion, hexafluoro phosphate ion, and aryl sulfonic-acid ion preferably.

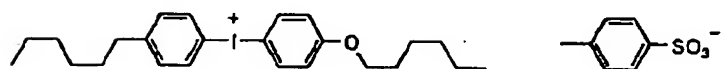
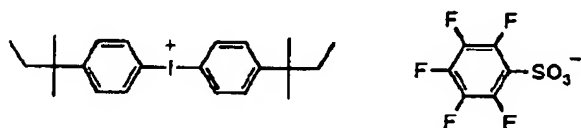
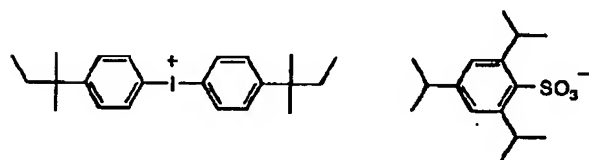
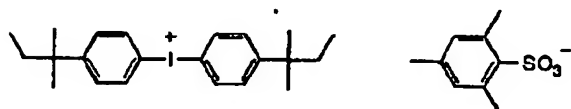
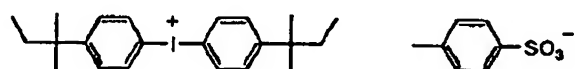
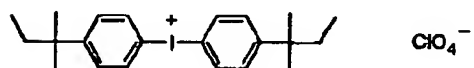
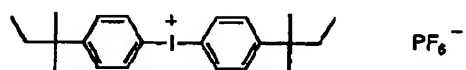
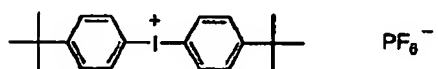
[0059] Ar21 shows the aryl group of 20 or less (the carbon number of a substituent is included) carbon atomic numbers which may have the substituent among a formula (V). As a desirable substituent, a halogen atom, a nitro group, the alkyl group of 12 or less carbon atomic numbers, the alkoxy group of 12 or less carbon atomic numbers, the aryloxy group of 12 or less carbon atomic numbers, the alkylamino radical of 12 or less carbon atomic numbers, the dialkylamino radical of 12 or less carbon atomic numbers, the arylamino radical of 12 or less carbon atomic numbers, or the diaryl amino group of 12 or less carbon atomic numbers is mentioned. Z21- expresses the counter ion of Z11- and homonymy.

[0060] among a formula (VI), even if R31, R32, and R33 are the same respectively, they may differ from each other, and they show the hydrocarbon group of 20 or less (the carbon number of a substituent is included) carbon atomic numbers which may have the substituent. As a desirable substituent, a halogen atom, a nitro group, the alkyl group of 12 or less carbon atomic numbers, the alkoxy group of 12 or less carbon atomic numbers, or the aryloxy group of 12 or less carbon atomic numbers is mentioned. Z31- expresses the counter ion of Z11- and homonymy.

[0061] In this invention, what was indicated by the following Japanese-Patent-Application-No. No. 310623 [ 11 to ] specification can be mentioned as an example of the onium salt which can be suitably used as a radical generating agent.

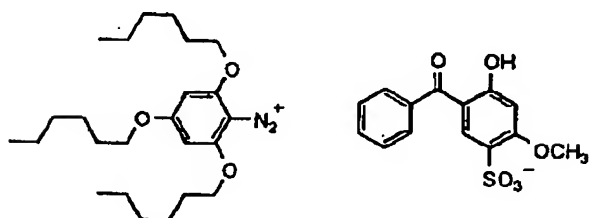
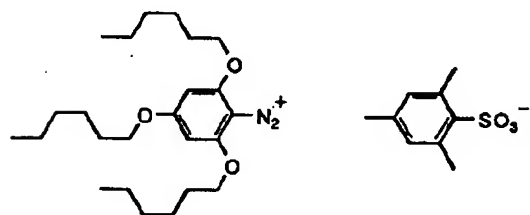
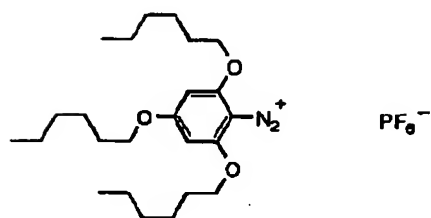
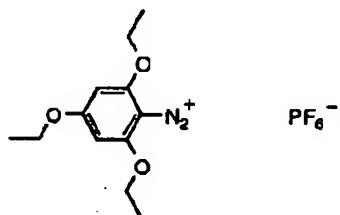
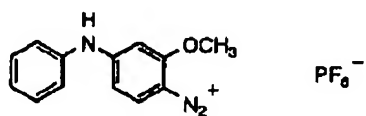
[0062]

[Formula 11]



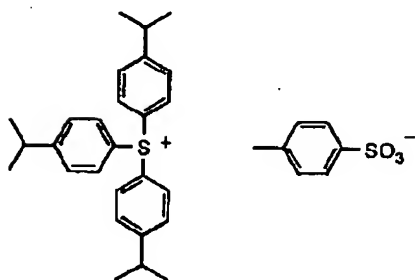
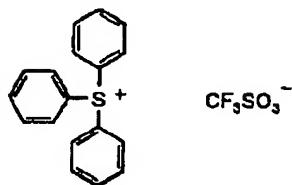
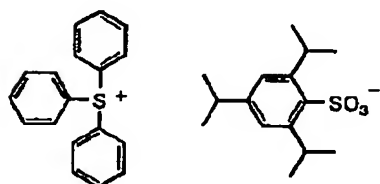
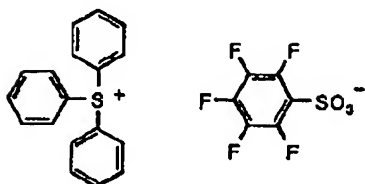
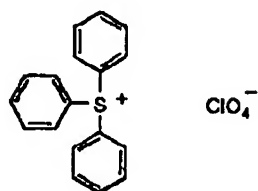
[0063]

[Formula 12]



[0064]

[Formula 13]



[0065] As for the pyrolysis mold radical generating agent used in this invention, it is desirable that absorption maximum wavelength is 400nm or less, and it is desirable that it is 360 morenm or less. Thus, the handling [ the negative-mold photosensitivity lithography version ] under a white light by making absorption wavelength into an ultraviolet-rays field. These pyrolyses mold radical generating agent can be especially added [ 0.5 ] from 0.1 in sensitization layer coating liquid at 1 to 20% of the weight of a rate preferably 30% of the weight 50% of the weight to all the non-volatile components of sensitization layer coating liquid. If sensibility becomes it low that an addition is less than 0.1 % of the weight and 50 % of the weight is exceeded, dirt will be generated in the non-image section at the time of printing. Only one sort may be used for these radical generating agents, and they may use two or more sorts together. Moreover, although these pyrolysis mold radical generating agents may be added in the same layer as other components, and another layer may be prepared and you may add there, adding in the same layer is more desirable.

[0066] In light or a thermal polymerization nature negative-mold sensitization layer desirable as a



sensitization layer of the negative-mold photosensitivity monotonous printing version of this invention, the component of others which were [ other than the above fundamental component ] further suitable for the application, the manufacture approach, etc. can be added suitably. Hereafter, it illustrates about a desirable additive.

In a [co-sensitizer] photopolymerization nature sensitization layer, the sensibility of this sensitization layer can be further raised by using a co-sensitizer. Although these mechanisms of action are not clear, many are considered based on the following chemical processes. That is, co-sensitizers (a radical, a peroxide, an oxidizing agent, reducing agent, etc.) react with various middle active species produced in process of the photoreaction started by the light absorption of the photopolymerization initiator (system) of point \*\*, and the addition polymerization reaction which follows it, and what generates a new activity radical is presumed. These react with a radical with low what (a) reduction is carried out and can generate an activity radical greatly, thing which (b) oxidization is carried out and can generate an activity radical, and (c) activity, and there is no accepted theory about whether it changes into a radical with more high activity, or to which [ these ] although it can classify into what acts as a chain transfer agent, each compound belongs in many cases.

[0067] (a) it has compound carbon-halogen association which is returned and generates an activity radical -- carbon-halogen association \*\*\*\* in compound:reduction and it is thought that an activity radical is generated. Specifically, trihalomethyl-s-triazine and trihalomethyl OKISA diazoles can use it suitably.

The compound which has nitrogen-nitrogen association: Nitrogen-nitrogen association \*\*\*\* in reduction and it is thought that an activity radical is generated. Specifically, hexaaryl biimidazole is used suitably.

The compound which has oxygen-oxygen association: Oxygen-oxygen association \*\*\*\* in reduction and it is thought that an activity radical is generated. Specifically, organic peroxide is used suitably.

Onium compound: Carbon-hetero association and oxygen-nitrogen association \*\*\*\* in reduction, and it is thought that an activity radical is generated. Specifically, diaryl iodonium salts, triarylsulfonium salts, N-alkoxy pyridinium (horse mackerel NIUMU) salts, etc. are used suitably.

a ferrocene -- an activity radical can be generated in iron arene complex:reduction.

[0068] (b) it oxidizes and an activity radical is generated -- carbon-hetero association \*\*\*\* in compound alkyl ate-complex:oxidization, and it is thought that an activity radical is generated. Specifically, thoria reel alkyl borate is used suitably.

Alkylamine compound: C-X association on the carbon which adjoined nitrogen by oxidization \*\*\*\*, and it is thought that an activity radical is generated. As X, a hydrogen atom, a carboxyl group, a trimethylsilyl radical, benzyl, etc. are suitable. Specifically, ethanolamines, N-phenylglycine, and N-trimethylsilyl methylaniline are mentioned.

Sulfur-containing yellow, an tin-containing compound: What transposed the nitrogen atom of above-mentioned amines to the sulfur atom and the tin atom can generate an activity radical according to the same operation. Moreover, the sensitization also according [ the compound which has an S-S bond ] to S-S \*\*\*\* is known.

[0069] alpha-permutation methyl carbonyl compound: By oxidization, joint \*\*\*\* between carbonyl-alpha carbon can generate an activity radical. Moreover, the operation with the same said of what changed carbonyl into the oxime ether is shown. Specifically, it is 2. - After reacting these and hydroxy amines to alkyl-1-[4-(alkylthio) phenyl]-2-morpholino Pronon -1 kind and a list, the oxime ether which etherified N-OH can be mentioned.

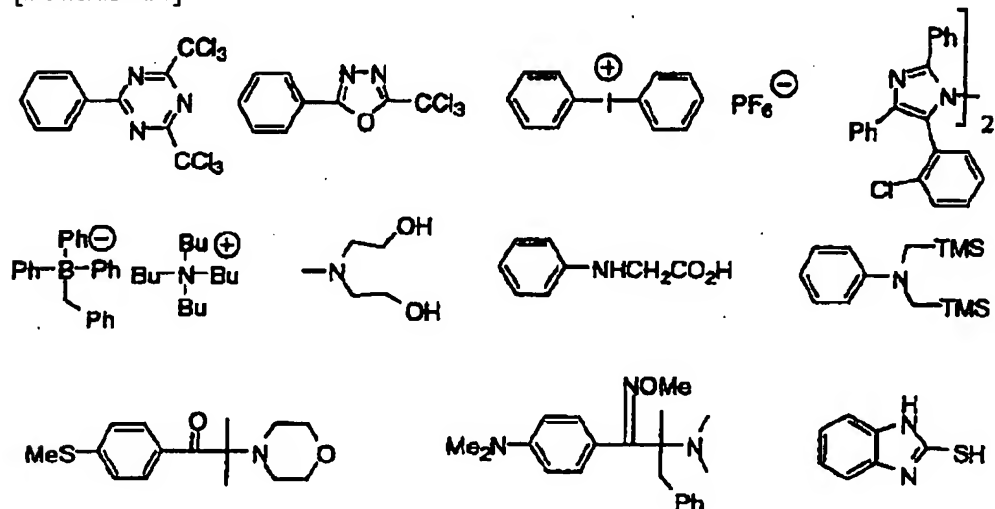
Sulfinate: An activity radical can be generated in reduction. A concrete target can mention aryl sulfinic acid sodium etc.

[0070] (c) Compound:, for example, the compound group which has SH, PH, SiH, and GeH in intramolecular, which reacts with a radical and acts on a high activity radical as conversion or a chain transfer agent is used. These carry out hydrogen supply at the radical kind of low activity, and after they generate a radical or oxidize, they can generate a radical by carrying out deprotonate. Specifically, 2-mercaptobenzimidazole is mentioned. Many more concrete examples of these co-sensitizers are

indicated as an additive aiming at the improvement in sensibility for example, in JP,9-236913,A. Although the part is illustrated below, there is that [ no ] by which what is used for the sensitization layer of the negative-mold photosensitivity monotonous printing version of this invention is limited to these.

[0071]

[Formula 14]



[0072] It is also possible to perform various chemical modification for improving the property of a sensitization layer further also about these co-sensitizers. For example, approaches, such as substituent installation for association with the radical generating PERT of sensitizing dye, titanocene, and an addition polymerization nature unsaturated compound and others, installation of a hydrophilic part, the improvement in compatibility, and crystal deposit control, substituent installation which raises adhesion, and polymer-izing, can be used. these co-sensitizers are independent -- or two or more sorts can be used together and it can use. the compound 100 weight section in which the amount used has an ethylene nature partial saturation double bond -- receiving -- the 0.05 - 100 weight section -- desirable -- 1 - 80 weight section -- the range of 3 - 50 weight section is still more preferably suitable.

[0073] [Polymerization inhibitor] In order to prevent the unnecessary thermal polymerization of the compound which has the ethylene nature partial saturation double bond in which a polymerization is possible during manufacture of a negative-mold photosensitivity constituent, or preservation in an especially desirable light or a thermal polymerization nature negative-mold sensitization layer as a sensitization layer of the negative-mold photosensitivity monotonous printing version of this invention, it is desirable to add a small amount of thermal polymerization inhibitor again. As suitable thermal polymerization inhibitor, hydroquinone, p-methoxy phenol, G t-butyl-p-cresol, pyrogallol, t-butyl catechol, a benzoquinone, 4,4'-thiobis (3-methyl-6-t-butylphenol), 2,2'-methylene bis (4-methyl-6-t-butylphenol), the first cerium salt of an N-nitroso phenyl hydroxy amine, etc. are mentioned. The addition of thermal polymerization inhibitor has about 0.01 % of the weight - about 5 desirable % of the weight to the weight of the non-volatile component in [ all ] a constituent. Moreover, if needed, in order to prevent the polymerization inhibition by oxygen, behenic acid, a higher-fatty-acid derivative like a behenic acid amide, etc. may be added, and you may make it unevenly distributed in the front face of a sensitization layer in process of desiccation after spreading. The addition of a higher-fatty-acid derivative has about 0.5 % of the weight - about 10 desirable % of the weight to the non-volatile component in [ all ] a constituent.

[0074] [Coloring agent] A color or a pigment may be further added for the purpose of the coloring in the sensitization layer of the negative-mold photosensitivity monotonous printing version of this invention. Thereby, the visibility after platemaking as a printing version and so-called proof comparison nature called image density measurement machine fitness can be raised. As a coloring agent, since many colors produce the fall of the sensibility of a photopolymerization system sensitization layer, especially as a

coloring agent, its use of a pigment is desirable. As an example, there are colors, such as pigments, such as phthalocyanine pigment, azo pigment, carbon black, and titanium oxide, ethyl violet, a crystal violet, azo dye, anthraquinone dye, and cyanine dye. The addition of a color and a pigment has about 0.5 % of the weight - about 5 desirable % of the weight to the non-volatile component in [ all ] a constituent.

[0075] In order to improve the physical properties of a hardening coat, an inorganic bulking agent and an additive with a plasticizer, the affinitizing agent in which the ink impression nature of a sensitization layer front face is raised, and it deals well-known in addition to this may be added to a [other additive] pan. As a plasticizer, there are dioctyl phthalate, didodecyl phthalate, triethylene glycol dicaprylate, dimethyl glycol phthalate, tricresyl phosphate, dioctyl adipate, dibutyl sebacate, a thoria cetyl glycerol, etc., and, generally it can add in 10 or less % of the weight of the range to the sum total weight of a giant-molecule binder and an addition polymerization nature compound. Moreover, addition of a UV initiator, a heat cross linking agent, etc. for strengthening the effectiveness of heating and exposure after the development aiming at the improvement in film on the strength (print durability) mentioned later can also be performed.

[0076] In case the above-mentioned sensitization layer is painted, the photopolymerization nature constituent of this sensitization layer component is melted to various organic solvents, and it is offered so that it may apply on this interlayer. As a solvent used here, an acetone, a methyl ethyl ketone, a cyclohexane, Ethyl acetate, ethylene dichloride, a tetrahydrofuran, toluene, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol wood ether, propylene glycol monomethyl ether, The propylene glycol monoethyl ether, an acetylacetone, a cyclohexanone, Diacetone alcohol, ethylene glycol monomethyl ether acetate, Ethylene glycol ethyl ether acetate, ethylene glycol mono-isopropyl ether, Ethylene-glycol-monobutyl-ether acetate, 3-methoxy propanol, Methoxy methoxy ethanol, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, diethylene-glycol wood ether, Diethylene-glycol diethylether, propylene-glycol-monomethyl-ether acetate, There are propylene glycol monoethyl ether acetate, 3-methoxy propyl acetate, N.N-dimethylformamide, dimethyl sulfoxide, gamma-butyrolactone, methyl lactate, ethyl lactate, etc. these solvents are independent -- or it can be mixed and used. And 2 - 50 % of the weight is suitable for the concentration of the solid content in a spreading solution.

[0077] As for the amount of covering of said sensitization layer, it is desirable to influence the sensibility of a sensitization layer, development nature, and the reinforcement and print durability of the exposure film, and to mainly choose suitably according to an application. Print durability becomes less enough when there are too few amounts of covering. In many [ too ], when sensibility falls and exposure takes time amount on the other hand, it is not desirable in order for a development to also take longer time amount. As a negative-mold photosensitivity monotonous printing version for scan exposure which are the main purposes of this invention, the range of about 0.1g/m<sup>2</sup> - about 10 g/m<sup>2</sup> is suitable for the amount of covering by the weight after desiccation. It is 0.5 - 5 g/m<sup>2</sup> more preferably.

[0078] As a base material of the negative-mold photosensitivity monotonous printing version of [base material] this invention, it can be conventionally used without limitation of the hydrophilic base material used for the well-known negative-mold photosensitivity monotonous printing version. That it is a tabular object stable in dimension the base material used preferably for example, paper and plastics (for example, polyethylene and polypropylene --) the paper which polystyrene etc. laminated, and a metal plate (for example, aluminum --) plastic film (for example, diacetyl cellulose --), such as zinc and copper A cellulose triacetate, cellulose propionate, a butanoic acid cellulose, a cellulose acetate butyrate, A cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, Paper or plastic film etc. with which the metal like the above, such as polypropylene, a polycarbonate, and a polyvinyl acetal, was laminated or vapor-deposited is contained. suitable [ if needed / for grant of a hydrophilic property, and the purpose, such as improvement in on the strength, ] to these front faces -- well-known -- physical and chemical preparation may be performed.

[0079] As an especially desirable base material, paper, polyester film, or an aluminum plate is mentioned, also in it, dimensional stability is good, and is comparatively cheap, and the aluminum plate which can offer the front face which was excellent in a hydrophilic property or reinforcement with

surface treatment as occasion demands is still more desirable. Moreover, the complex sheet with which the aluminium sheet was combined on a polyethylene terephthalate film which is indicated by JP,48-18327,B is also desirable.

[0080] An aluminum plate is a metal plate which uses aluminum stable in dimension as a principal component, and aluminum besides a pure aluminium plate is used as a principal component, and it is chosen from the alloy plate containing the different element of a minute amount, the plastic film with which aluminum (alloy) was laminated or vapor-deposited, or paper. In the following explanation, the substrate which consists of the aluminum or the aluminium alloy mentioned above is named an aluminum substrate generically, and is used. There are silicon, iron, manganese, copper, magnesium, chromium, zinc, a bismuth, nickel, titanium, etc. in the different element contained in said aluminium alloy, and the content of the different element in an alloy is 10 or less % of the weight. In this invention, although a pure aluminium plate is suitable, since manufacture on a refinement technique is difficult for completely pure aluminum, a different element may be contained slightly. Thus, the presentation is not specified and the aluminum plate applied to this invention is the thing of the material of well-known official business, for example, JIS, from the former. A 1050 JIS A 1100 JIS A 3103 JIS A 3005 etc. can be used suitably. Moreover, the thickness of the aluminum substrate used for this invention is about 0.1mm - about 0.6mm. This thickness can be suitably changed by the magnitude of a printing machine, the magnitude of the printing version, and a user's hope. The below-mentioned substrate surface treatment may be suitably performed to an aluminum substrate if needed. Of course, it does not need to be given.

[0081] The [surface roughening process] surface roughening process approach has mechanical surface roughening which is indicated by JP,56-28893,A, chemical etching, an electrolysis grain, etc. a mechanical surface roughening method like the electrochemical-surface-roughening approach which carries out surface roughening still more nearly electrochemically in a hydrochloric acid or the nitric-acid electrolytic solution and the wire brush grain method for scratching an aluminum front face with a metal wire, the pole grain method which carries out an aluminum front face to a polish ball by graining by the abrasive material, and the brush grain method which carries out surface roughening of the front face to a nylon brush by the abrasive material can be used, and independent in the above-mentioned surface roughening approach -- or it can also combine and use. The approach used for surface roughening useful also in it is an electrochemical process which carries out surface roughening chemically in a hydrochloric acid or the nitric-acid electrolytic solution, and quantity of electricity is the range of 50 C/dm<sup>2</sup> - 400 C/dm<sup>2</sup> at the time of the anode plate for which are suitable. It is still more specifically desirable among the electrolytic solution containing 0.1 - 50% of hydrochloric acid, or a nitric acid to perform alternating current and/or direct-current electrolysis for the temperature of 20-80 degrees C, and 1 second to time amount 30 minutes on condition that current density 100 C/dm<sup>2</sup> - 400 C/dm<sup>2</sup>.

[0082] Thus, the aluminum substrate which carried out the surface roughening process may be chemically etched with an acid or alkali. The etching agents used suitably are caustic alkali of sodium, sodium carbonate, sodium aluminate, meta-sodium silicate, a sodium phosphate, a potassium hydroxide, a lithium hydroxide, etc., and the range where concentration and temperature are desirable is 20-100 degrees C 1 to 50%, respectively. After etching, in order to remove the dirt (smut) which remains on a front face, pickling is performed. As for the acid used, a nitric acid, a sulfuric acid, a phosphoric acid, a chromic acid, fluoric acid, fluoroboric acid, etc. are used. The approach of carrying out alkali etching indicated by the approach and JP,48-28123,B which are contacted to 15 - 65% of the weight of a sulfuric acid with a temperature of 50-90 degrees C which is preferably indicated by JP,53-12739,A especially as a desmutting art after electrochemical-surface-roughening processing is mentioned. If center line average-of-roughness-height Ra of a processing side is 0.2-0.5 micrometers after being processed as mentioned above, especially approach conditions will not be limited.

[0083] [Anodizing] Anodizing is made after that by the aluminum substrate which was processed as mentioned above and formed the oxide layer. the water solution of anodizing of a sulfuric acid, phosphoric acid, oxalic acid or boric acid / sodium borate is independent -- or two or more kinds are

combined and it is used as a principal component of an electrolytic bath. Under the present circumstances, of course, the component usually contained in aluminum alloy plate, an electrode, tap water, an underground water, etc. at least may be contained in the electrolytic solution. Furthermore, the 2nd and 3rd component may be added. With the 2nd and 3 component here, anions, such as a cation, nitrate ion and carbonate ion, a chlorine ion, phosphoric-acid ion, fluorine ion, sulfite ion, titanate ion, silicate ion, and boric acid ion, may be mentioned to metal ion, ammonium ion, etc., such as Na, K, Mg, Li, calcium, Ti, aluminum, V, Cr, Mn, Fe, Co, nickel, Cu, and Zn, and about 0-10000 ppm may be contained as the concentration. Although there is especially no limitation in the conditions of anodizing, it is 30-500g [ l. ] /and 10-70 degrees C of processing solution temperature preferably, and is processed by a direct current or alternating current electrolysis in the range of current density 0.1 - 40 A/m<sup>2</sup>. The range of the thickness of the anodic oxide film formed is 0.5-1.5 micrometers. It is the range of 0.5-1.0 micrometers preferably. Processing conditions must be chosen so that 5-10nm and a pore consistency may go [ the diameter of pore of the micro pore to which the base material produced by the above processing exists in an anodic oxide film ] into the range of  $8 \times 10^{15}$  to  $2 \times 10^{16}$  pieces/m<sup>2</sup>.

[0084] As hydrophilization processing of said support surface, a large well-known approach is applicable. As desirable processing, hydrophilization processing by silicate or polyvinyl phosphonic acid is performed especially. a coat -- as Si or a P yuan quantum -- 2 - 40 mg/m<sup>2</sup> -- it is more preferably formed by 4-30mg/m<sup>2</sup>. Coverage can be measured by the ray light X-ray analysis.

[0085] An alkali-metal silicate or polyvinyl phosphonic acid is 2 - 15 % of the weight preferably one to 30% of the weight, and the above-mentioned hydrophilization processing is carried out by immersing the aluminum substrate with which the anodic oxide film was formed for 0.5 to 120 seconds at 15-80 degrees C in the water solution whose pH of 25 degrees C is 10-13.

[0086] As an alkali-metal silicate used for said hydrophilization processing, a sodium silicate, a potassium silicate, a silicic-acid lithium, etc. are used. As a hydroxide used in order to make high pH of an alkali-metal silicate water solution, there are a sodium hydroxide, a potassium hydroxide, a lithium hydroxide, etc. in addition, the above-mentioned processing liquid -- the [ an alkaline-earth-metal salt or ] -- an IVB group metal salt may be blended. As an alkaline earth metal salt, water-soluble salts, such as a calcium nitrate, a strontium nitrate, a magnesium nitrate, a nitrate like a barium nitrate, and a sulfate, a hydrochloride, phosphate, acetate, an oxalate, a borate, are mentioned. the -- as an IVB group metal salt, a titanium tetrachloride, a titanium trichloride, a titanium fluoride potassium, a titanium oxalate potassium, sulfuric-acid titanium, 4 titanium iodide, a chlorination zirconium dioxide, a zirconium dioxide, zirconium oxychloride, a zirconium tetrachloride, etc. can be mentioned.

[0087] the [ an alkaline-earth-metal salt or ] -- an IVB group metal salt is independent -- or two or more sorts can be used, combining. The desirable range of these metal salts is 0.01 - 10 % of the weight, and the still more desirable range is 0.05 - 5.0 % of the weight. Moreover, silicate electrodeposition which is indicated by the U.S. Pat. No. 3,658,662 specification is also effective. The base material which gave an electrolysis grain which is indicated by JP,46-27481,B, JP,52-58602,A, and JP,52-30503,A, and the surface treatment which combined the above-mentioned anodizing and hydrophilization processing are also useful.

[0088] An interlayer may be prepared in the negative-mold photosensitivity monotonous printing version in [interlayer] this invention in order to improve the adhesion and dirt nature between a sensitization layer and a substrate. As such an interlayer's example, JP,50-7481,B, JP,54-72104,A, JP,59-101651,A, JP,60-149491,A, JP,60-232998,A, JP,3-56177,A, JP,4-282637,A, JP,5-16558,A, JP,5-246171,A, JP,7-159983,A, JP,7-314937,A, JP,8-202025,A, JP,8-320551,A, JP,9-34104,A, JP,9-236911,A, JP,9-269593,A, JP,10-69092,A, JP,10-115931,A, JP,10-161317,A, JP,10-260536,A, JP,10-282682,A, JP,11-84674,A, Japanese Patent Application No. No. 225335 [ eight to ], Japanese Patent Application No. No. 270098 [ eight to ], Japanese Patent Application No. No. 195863 [ nine to ], Japanese Patent Application No. No. 195864 [ nine to ], Japanese Patent Application No. No. 89646 [ nine to ], Japanese Patent Application No. No. 106068 [ nine to ], Japanese Patent Application No. No. 183834 [ nine to ], Japanese Patent Application No. No. 264311 [ nine to ], Japanese Patent Application No. No. 127232 [ nine to ], Japanese Patent Application No. No. 245419 [ nine to ], The thing of a

publication can be mentioned to Japanese Patent Application No. No. 127602 [ ten to ], Japanese Patent Application No. No. 170202 [ ten to ], Japanese Patent Application No. No. 36377 [ 11 to ], Japanese Patent Application No. No. 165861 [ 11 to ], Japanese Patent Application No. No. 284091 [ 11 to ], an application for patent No. 14697 [ 2000 to ], etc.

[0089] In order to expose in atmospheric air for the negative-mold photosensitivity monotonous printing version which has the light or the thermal polymerization nature negative-mold sensitization layer which is the desirable gestalt of [protective layer] this invention, for it, it is usually desirable to prepare a protective layer further on the above-mentioned sensitization layer. A protective layer prevents mixing to the sensitization layer of low molecular weight compounds, such as oxygen and an alkali, which exists in the atmospheric air which checks the image formation reaction produced by exposure in a sensitization layer, and enables exposure in atmospheric air. Therefore, the property which such a protective layer is expected is that the permeability of low molecular weight compounds, such as oxygen, is low, and, as for transparency of the light used for exposure, it is still more desirable that real inhibition is not carried out, but it excels in adhesion with a sensitization layer, and can remove easily at the development process after exposure. Such a device about a protective layer is made conventionally, and is indicated in detail by United States patent No. 3,458,311 and JP,55-49729,A. It is good to use the water soluble polymer compound which was comparatively excellent in crystallinity as an ingredient which can be used for a protective layer, for example, and although water-soluble polymers, such as polyvinyl alcohol, a polyvinyl pyrrolidone, acid celluloses, gelatin, gum arabic, and polyacrylic acid, are known, specifically, use polyvinyl alcohol as a principal component gives the best results in basic property, such as oxygen cutoff nature and development removal nature, among these. As long as the polyvinyl alcohol used for a protective layer contains the non-permuted vinyl alcohol unit for having required oxygen cutoff nature and water solubility, the part may be permuted by ester, the ether, and the acetal. Moreover, the part may have other copolymerization components similarly. As an example of polyvinyl alcohol, it hydrolyzes 71 to 100%, and molecular weight can mention the thing of the range of 300 to 2400. Specifically PVA-105 by Kuraray Co., Ltd., PVA-110, PVA-117, PVA-117H, PVA-120, PVA-124, PVA-124H, PVA-CS, PVA-CST, PVA-HC, PVA-203, PVA-204, PVA-205, PVA-210, PVA-217, PVA-220, PVA-224, PVA-217EE, PVA-217E, PVA-220E, PVA-224E, PVA-405, PVA-420, PVA-613, and L-8 grade are mentioned.

[0090] The component (selection of PVA, use of an additive) of a protective layer, coverage, etc. are chosen in consideration of others and fogging nature, and adhesion and damage resistance. [ nature / oxygen cutoff nature and / development removal ] Oxygen cutoff nature becomes high and is so advantageous that thickness is so so thick that the rate of hydrolysis of PVA generally used is high (that the non-permuted vinyl alcohol unit content in a protective layer is high) in respect of sensibility. However, if oxygen cutoff nature is raised extremely, the problem of being as \*\*\*\* of unnecessary fogging and a streak arising at the time of image exposure \*\*\*\* [ , and ] will be produced. [ that an unnecessary polymerization reaction arises at the time of - raw preservation at the time of manufacture ] Moreover, adhesion with the image section and damage resistance are also very important on the handling of a version. That is, if the laminating of the layer of the hydrophilic property which consists of a water-soluble polymer is carried out to an oleophilic sensitization layer, it will be easy to generate the film exfoliation by the lack of adhesive strength, and an exfoliation part will cause the defect of poor film hardening by polymerization inhibition of oxygen. On the other hand, various proposals are made that the adhesive property between two-layer [ these ] should be improved. For example, it is indicated by U.S. Pat. No. 292,501 and U.S. Pat. No. 44,563 by mixing an acrylic emulsion or a water-insoluble nature vinyl-pyrrolidone-vinyl acetate copolymer 20 to 60% of the weight, and carrying out a laminating on a sensitization layer into the hydrophilic polymer which mainly consists of polyvinyl alcohol, that sufficient adhesive property is acquired. To the protective layer in this invention, each of these well-known techniques is applicable. The method of application of such a protective layer is indicated in detail by U.S. Pat. No. 3,458,311 and JP,55-49729,A, for example.

[0091] In addition, as a platemaking process for engraving the lithography version, the whole surface may be heated before exposure and during exposure from exposure before development if needed from



the negative-mold photosensitivity monotonous printing version of this invention. By such heating, the image formation reaction in a sensitization layer is promoted, and advantages, such as improvement in sensibility or print durability and stabilization of sensibility, may arise. Furthermore, it is also effective to perform whole surface afterbaking or complete exposure to the image after development for the purpose of improvement in image reinforcement and print durability. Usually, it is desirable to perform heating before development on mild conditions 150 degrees C or less. If temperature is too high, the problem of even the non-image section fogging will be produced. Very strong conditions are used for heating after development. Usually, it is the range of 200-500 degrees C. If temperature is low, sufficient image potentiation will not be obtained, but in being too high, it produces problems, such as degradation of a base material and a pyrolysis of the image section.

[0092] The exposure approach of the negative-mold photosensitivity monotonous printing version of this invention can be used without a limit of a well-known approach. The desirable wavelength of the light source is 300nm to 1200nm, and the light source of laser various kinds is specifically suitable for it. Any, such as an inside drum method, an outside drum method, and a flatbed method, are sufficient as an exposure device. Moreover, although [ neutral water or the neutral weak alkaline water ] the sensitization layer component of the negative-mold photosensitivity monotonous printing version of this invention is using a water-soluble high thing and it is meltable, after loading on a printing machine, the negative-mold photosensitivity monotonous printing version of such a configuration is on board, and can also hold a method called exposure-development.

[0093] Moreover, as an exposure beam of light of others to the negative-mold photosensitivity monotonous printing version of this invention, extra-high voltage, high pressure, a medium voltage, each low-pressure mercury-vapor lamp, a chemical lamp, a carbon arc lamp, a xenon LGT, a metal halide LGT, various visible and ultraviolet laser lamps, a fluorescent lamp, a tungsten LGT, sunlight, etc. can be used.

[0094] After being exposed, the development of the negative-mold photosensitivity monotonous printing version of this invention is carried out. Especially as a developer used for this development, a with a pH of 14 or less alkali water solution is desirable, and the alkali water solution of pH 8-12 which contains an anion system surfactant more preferably is used. For example, inorganic alkali chemicals, such as the third sodium phosphate, this potassium, this ammonium, sodium diphosphate, this potassium, this ammonium, a sodium carbonate, this potassium, this ammonium, a sodium hydrogencarbonate, this potassium, this ammonium, the sodium borate, this potassium, this ammonium, a sodium hydroxide, this ammonium, this potassium, and this lithium, are mentioned. Moreover, organic alkali chemicals, such as monomethylamine, dimethylamine, a trimethylamine, a monoethyl amine, diethylamine, triethylamine, mono-isopropylamine, diisopropylamine, a triisopropyl amine, n butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and a pyridine, are also used. These alkali chemicals are used combining independent or two sorts or more.

[0095] Moreover, in the development of the negative-mold photosensitivity monotonous printing version of this invention, although added into a developer 1 - 20 % of the weight of anionic surface active agents, it is more preferably used at 3 - 10 % of the weight. If too few, development nature will get worse, and if many [ too ], the evil of reinforcement of an image, such as abrasion resistance, deteriorating will come out. As an anionic surface active agent, for example The sodium salt of lauryl alcohol sulfate, The ammonium salt of lauryl alcohol sulfate, the sodium salt of octyl alcohol sulfate, For example, sodium salt of an isopropyl naphthalene sulfonic acid, sodium salt of an isobutyl naphthalene sulfonic acid, The sodium salt of polyoxy-ethylene-glycol mono-naphthyl ethereal sulfate ester, Alkylaryl sulfonates, such as sodium salt of dodecylbenzenesulfonic acid, and sodium salt of a meta-nitrobenzene sulfonic acid, The higher-alcohol sulfates of the carbon numbers 8-22, such as the 2nd sodium alkyl sulfate Fatty alcohol phosphate, such as sodium salt of cetyl alcohol phosphoric ester For example, the sulfonates of alkylamide, such as  $C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na$  For example, the sulfonates of dibasicity aliphatic series ester, such as sodium sulfo succinic-acid dioctyl ester and sodium sulfo succinic-acid dihexyl ester, are contained.

[0096] An organic solvent which is mixed with water, such as benzyl alcohol, if needed may be added to a developer. As an organic solvent, about 10 or less % of the weight of the thing is suitable, and the solubility to water is preferably chosen from 5 or less % of the weight of a thing. For example, 1-phenyl ethanol, 2-phenyl ethanol, 3-phenylpropanol, 1, 4-phenyl butanol, 2, and 2-phenyl butanol, 1, 2-phenoxyethanol, 2-benzyloxy ethanol, o-methoxybenzyl alcohol, m-methoxybenzyl alcohol, para methoxybenzyl alcohol, benzyl alcohol, a cyclohexanol, 2-methyl cyclo hexanol, 4-methyl cyclo hexanol, 3-methyl cyclo hexanol, etc. can be mentioned. 1 - 5 % of the weight is suitable for the content of an organic solvent to the AUW of the developer at the time of use. As for the amount of an anionic surface active agent, it is desirable to make it increase as the amount used has as close relation as the amount of the surfactant used and the amount of an organic solvent increases. This is in a condition with few amounts of an anionic surface active agent, and is because an organic solvent does not dissolve, therefore it becomes impossible to expect reservation of good development nature, when many amounts of an organic solvent are used.

[0097] Furthermore, a defoaming agent and an additive like a water softener can also be made to contain if needed. As a water softener, for example Polyphosphates, such as Na<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, Na<sub>5</sub>P<sub>3</sub>O<sub>3</sub>, Na<sub>3</sub>P<sub>3</sub>O<sub>9</sub>, Na<sub>2</sub>O<sub>4</sub>P(NaO<sub>3</sub>P) PO<sub>3</sub>Na<sub>2</sub>, and Calgon (polymetaphosphate sodium), For example, ethylene-diamine-tetraacetic acid, its potassium salt, its sodium salt; Diethylenetriaminepentaacetic acid, The potassium salt, sodium salt; A triethylenetetramine hexa acetic acid, The potassium salt, its sodium salt; A hydroxyethyl ethylene DIAMINTORI acetic acid, The potassium salt, its sodium salt; Nitrilotriacetic acid, its potassium salt, The sodium salt; 1, a 2-diamino cyclohexane tetra-acetic acid, its potassium salt, The sodium salt; 1, a 3-diamino-2-propanol tetra-acetic acid, Other 2-phosphono butane tricarboxylic acid of amino polycarboxylic acid, such as the potassium salt and its sodium salt - 1, 2, 4, potassium salt of those, The sodium salt; 2 1 phosphono butanone tricarboxylic acid - 2, 3, 4, potassium salt of those, The sodium salt; 1-phosphono ethane tricarboxylic acid - 1, 2, 2, potassium salt of those, The sodium salt; organic phosphonic acid, such as 1-hydroxy ethane -1, 1-diphosphonic acid, its potassium salt, its sodium salt; friend NOTORI (methylene phosphonic acid), its potassium salt, and its sodium salt, can be mentioned. Although the optimal amount of such a water softener changes according to the degree of hardness of hard water used, and its amount used, it is made to contain it in 0.01 - 0.5% of the weight of the range more preferably 0.01 to 5% of the weight generally in the developer at the time of use.

[0098] Furthermore, since a developer gets fatigued according to throughput in developing this negative-mold photosensitivity monotonous printing version using an auto-processor, a throughput may be recovered using a replenisher or a fresh developer. In this case, it is desirable to supply with the approach indicated by U.S. Pat. No. 4,882,246. Moreover, the developer indicated by each official report of JP,50-26601,A, 58-54341, JP,56-39464,B, 56-42860, and 57-7427 is also desirable.

[0099] Thus, after treatment of the negative-mold photosensitivity monotonous printing version by which the development was carried out is carried out with the desensitization liquid containing the rinse and gum arabic containing rinsing water, a surface active agent, etc., a starch derivative, etc. as indicated by each official report, such as JP,54-8002,A, 55-115045, and 59-58431. It can use for the after treatment of the negative-mold photosensitivity monotonous printing version of this invention combining various these processings. the lithography version obtained by such processing is hung on the offset press -- having -- many -- it is used for printing of several sheets. At the time of printing, as a plate cleaner used for the dirt removal on a version, the plate cleaner for PS plates known conventionally is used, for example, CL-1, CL-2, CP, CN-4, CN, CG-1, PC-1, SR, IC (Fuji Photo Film Co., Ltd. make), etc. are mentioned.

[0100]

[Example] Hereafter, although an example explains this invention, this invention is not limited to these.

[0101] (Synthetic example 1) cis-1, 2-cyclohexane dicarboxylic acid anhydride (308.3g), the methacrylic acid (2-hydroxyethyl) (273.3g), and 4-(dimethylamino) pyridine (4.9g) were added to the acetone (1,000ml), and heating reflux was carried out for 5 hours. After distilling off an acetone under reduced pressure, 1 convention hydrochloric acid (500ml) and ethyl acetate (2,000ml) were added, and the extract was performed. After saturation brine (500ml) washed the organic layer twice, sulfuric



anhydride magnesium (100g) was added, and was put for 1 hour, and dehydration processing was carried out. After carrying out magnesium sulfate a \*\* exception, when the bottom ethyl acetate of reduced pressure was distilled off, the white solid-state was obtained. After grinding this, after agitating for 2 hours in addition to water (2,000ml), the white solid-state (518.9g) of 2-[2-(methacryloyloxy)ethoxycarbonyl] cyclohexane carboxylic acid was obtained by drying a \*\* exception.

[0102] (Synthetic example 2) It was dropped at it at 70 degrees C under the nitrogen air current, having propylene-glycol-monomethyl-ether (310g) covered [ of methacrylic-acid allyl compound (35.8g), 2-[2-(methacryloyloxy)ethoxycarbonyl] cyclohexane-carboxylic-acid / which was obtained in the synthetic example 1 / (33.0g) and 2, and 2'-azobis (2,4-dimethylvaleronitrile) (0.99g) ] it over propylene glycol monomethyl ether (310g) for 2.5 hours. It agitated at 70 more degrees C after dropping termination for 2 hours. After cooling radiationally, this solution was fed into the water (4,000ml) agitated violently, and was agitated for further 1 hour. The binder polymer (P-1) (66.8g) given in Table 1 was obtained by drying the white fine particles which deposited a \*\* exception. In polystyrene conversion, the weight average molecular weight of this polymer measured with the gel par MITESHON chromatography method was 46,000, and the acid number was 1.72 meq/g.

[0103] (P-30) was similarly obtained from Table 1 and a binder polymer (P-2) given in Table 2.

[0104]

[Table 1]

表 1

バインダー ポリマー	一般式 (I) で表される 繰り返し単位	その他の 共重合成分	共重合モル比 (仕込み)	分子量 (万)	酸価 (meq/g)
P-1	PC-1	POC-1	29/71	4.6	1.72
P-2	PC-2	POC-1	35/65	6.2	2.00
P-3	PC-3	POC-1	26/74	3.6	1.50
P-4	PC-3	POC-1	32/68	6.2	1.78
P-5	PC-4	POC-1	28/72	3.7	1.55
P-6	PC-6	POC-1	40/60	11.5	2.10
P-7	PC-8	POC-1	30/70	4.8	1.75
P-8	PC-9	POC-1	15/85	0.9	0.98
P-9	PC-10	POC-1	29/71	4.8	1.72
P-10	PC-12	POC-1	23/77	3.8	1.43
P-11	PC-13	POC-1	27/73	3.9	1.60
P-12	PC-14	POC-1	8/92	2.4	1.15
P-13	PC-16	POC-1	22/78	4.1	1.30
P-14	PC-17	POC-1	30/70	8.4	1.58
P-15	PC-18	POC-1	25/75	4.5	1.41

[0105]

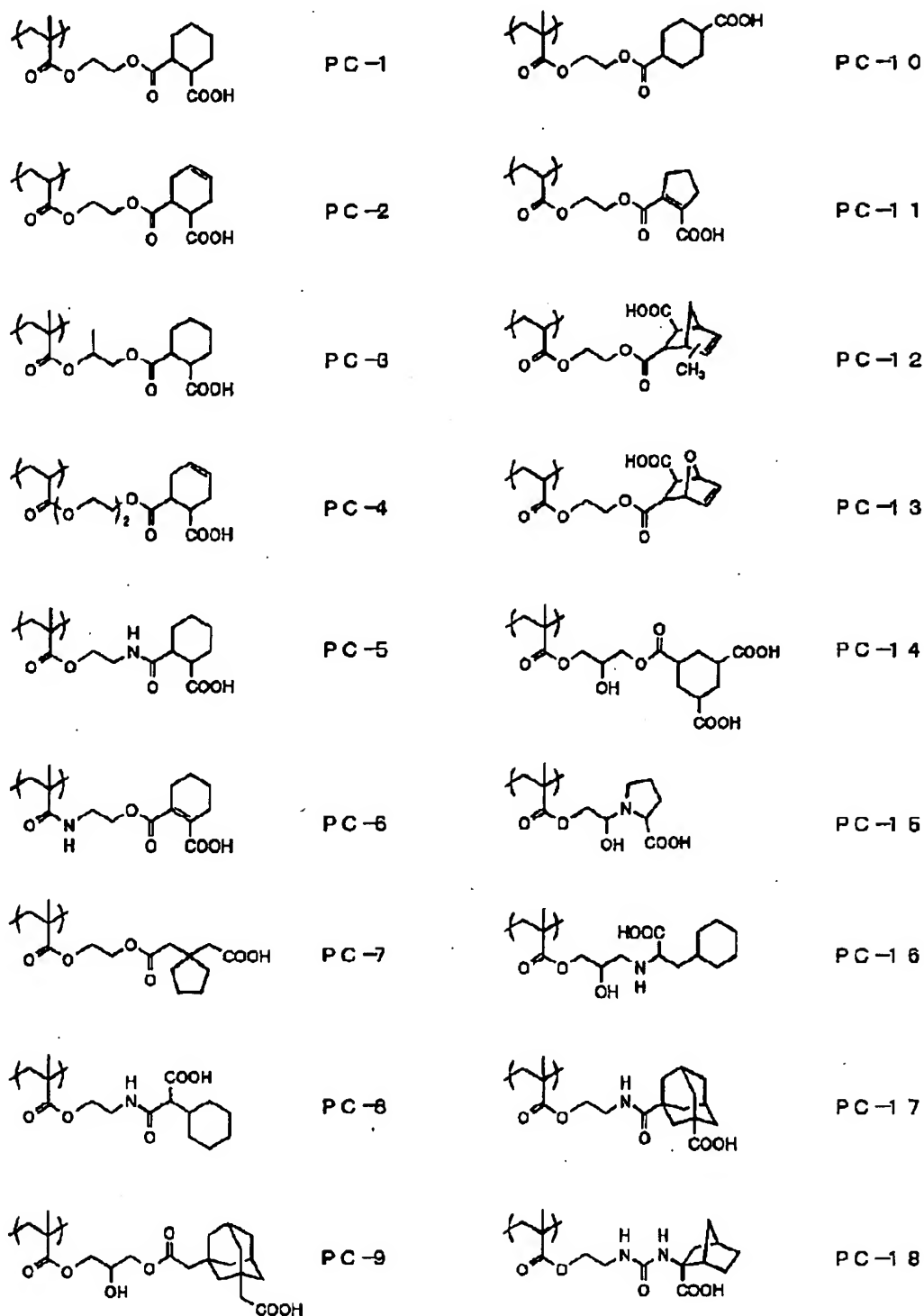
[Table 2]

表 2

バインダー ポリマー	一般式 (I) で表される 繰り返し単位	その他の共重合成分		共重合モル比 (仕込み)	分子量 (万)	酸価 (meq/g)
P-16	PC-1	POC-1	POC-2	29/51/20	4.6	1.72
P-17	PC-2	POC-2	POC-3	32/50/18	5.2	1.69
P-18	PC-2	POC-3	POC-4	19/45/36	6.2	1.74
P-19	PC-3	POC-2	POC-5	20/40/40	0.9	1.13
P-20	PC-4	POC-5	POC-6	32/50/18	4.5	1.74
P-21	PC-5	POC-1	POC-7	40/43/17	12.3	2.70
P-22	PC-7	POC-1	POC-8	34/55/11	9.7	2.22
P-23	PC-9	POC-2	POC-4	30/50/20	2.0	1.34
P-24	PC-11	POC-2	POC-8	18/60/22	6.5	1.89
P-25	PC-12	POC-5	POC-6	27/53/20	3.9	1.63
P-26	PC-13	POC-3	POC-8	15/65/20	6.3	2.17
P-27	PC-15	POC-2	POC-7	23/58/19	4.4	2.07
P-28	PC-17	POC-1	POC-7	33/55/12	5.6	2.12
P-29	PC-17	POC-5	POC-8	30/60/10	6.1	2.01
P-30	PC-18	POC-4	POC-7	25/40/35	7.6	3.22

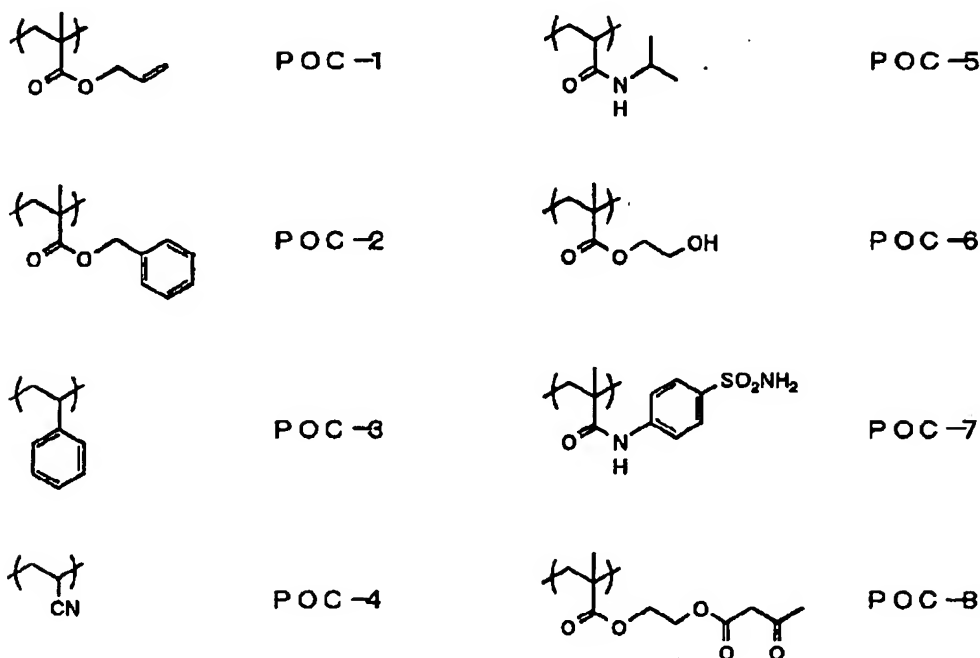
[0106]

[Formula 15]



[0107]

[Formula 16]



[0108] (Examples 1-20, examples 1-3 of a comparison) The negative-mold photosensitivity monotonous printing version was produced in the following procedures, and the printing engine performance was evaluated. A result is shown in Table 3.

[0109] JIS with 0.24mm [ in [creation of base material] thickness ], and a width of face of 1030mm A It processed continuously as follows using 1050 aluminum plates.

(a) The rotating roller-like nylon brush performed mechanical surface roughening, supplying them on the surface of an aluminum plate using existing mechanical surface roughening equipment having used the abrasive material (PAMISU) of specific gravity 1.12, and suspension of water as polish slurry liquid. 40-45-micrometer maximum grain size of the mean particle diameter of an abrasive material was 200 micrometers. The quality of the material of a nylon brush used 6-10 nylon, and the diameter of 50mm of hair length and hair was 0.3mm. The nylon brush transplanted hair so that a hole might be made in the cylinder made from phi300mm stainless steel and it might become dense. Three rotation brushes were used. The distance of two support rollers (phi200mm) of the brush lower part was 300mm. The brush roller was pressed down until the load of the drive motor made to rotate a brush became 7kw plus to the load before pressing down a brush roller to an aluminum plate. The hand of cut of a brush was the same as the migration direction of an aluminum plate, and the rotational frequency was 200rpm.

[0110] (b) Etching processing according an aluminum plate to a spray was performed at 2.6 % of the weight of caustic-alkali-of-sodium concentration, the aluminum ion concentration of 6.5 % of the weight, and the temperature of 70 degrees C, and 13g /of aluminum plates was dissolved two times m. Rinsing by the spray was performed after that.

(c) The 1 % of the weight water solution (it contains 0.5 % of the weight of aluminum ion) with a temperature of 30 degrees C of nitric-acid concentration performed the desmut treatment by the spray, and it rinsed by the spray after that. The waste fluid of the process which performs electrochemical surface roughening using an alternating current in a nitric-acid water solution was used for the nitric-acid water solution used for said De Dis Matt.

[0111] (d) The electrochemical surface roughening process was continuously performed using the alternating voltage of 60 Hz. The electrolytic solution at this time was 40 degrees C in the 1 % of the weight water solution (it contains 0.5 % of the weight of aluminum ion, and 0.007 % of the weight of ammonium ion) of nitric acids, and temperature. As for AC power supply, the time amount TP until a current value reaches a peak from zero performed the surface roughening process electrochemical as a counter electrode for the carbon electrode using 2msec(s), the duty ratio 1:1, and the trapezoid square wave alternating current. The ferrite was used for the auxiliary anode. As for 30 A/dm<sup>2</sup> and quantity of

electricity, the aluminum plate of current density was 255C/cm<sup>2</sup> in total of quantity of electricity at the time of an anode plate at the peak value of a current. 5% which flows from a power source of the current was made to shunt toward an auxiliary anode. Then, rinsing by the spray was performed.

[0112] (e) 26 % of the weight of caustic-alkali-of-sodium concentration and 6.5 % of the weight of aluminum ion concentration performed etching processing according an aluminum plate to a spray at 32 degrees C, the aluminum plate was dissolved two times 0.2 g/m, removal of the smut component which makes a subject the aluminum hydroxide generated when electrochemical surface roughening was performed using the alternating current of the preceding paragraph, and the edge part of the generated pit were dissolved, and the edge part was smoothed. It rinsed by the spray after that.

(f) The 25 % of the weight water solution (aluminum ion is included 0.5% of the weight) with a temperature of 60 degrees C of sulfuric-acid concentration performed the desmut treatment by the spray, and rinsing by the spray was performed after that.

[0113] (g) Anodizing was performed using the anodic oxidation equipment (the 2.4m each of the 6m [ of the first and second electrolysis division managers ] each, 3m [ of the first electric supply division managers ], 3m [ of the second electric supply division managers ], first, and second electric supply electrode length) of the existing two-step electric supply electrolysis approach at the sulfuric-acid concentration of 170g (aluminum ion is included 0.5% of the weight)/l. of the electrolysis section, and the temperature of 38 degrees C. Rinsing by the spray was performed after that. At this time, in anodic oxidation equipment, the current from a power source flows to the first electric supply electrode prepared in the first electric supply section, flows to tabular aluminum through the electrolytic solution, makes the front face of tabular aluminum generate an oxide film in the first electrolysis section, passes along the electrolysis electrode prepared in the first electric supply section, and returns to a power source. On the other hand, although the current from a power source flows to the second electric supply electrode prepared in the second electric supply section, flows to tabular aluminum through the electrolytic solution similarly and makes the front face of tabular aluminum generate an oxide film in the second electrolysis section. Quantity of electricity to which electric power is supplied by the second electric supply section from a power source was the same as quantity of electricity to which electric power is supplied by the first electric supply section from a power source, and the electric supply current density in the oxide film side in the second electric supply section was about 25 A/dm<sup>2</sup>. In the second electric supply section, electric power will be supplied from the oxide film side of 1.35 g/m<sup>2</sup>. The final amount of oxide films was 2.7 g/m<sup>2</sup>. The aluminum base material so far is set to [AS-1].

[0114] Silicate processing was performed in order to raise the hydrophilic property as the printing version non-image section to a [hydrophilization processing] aluminum base material [AS-1].

Processing was \*\*\*\*(ed) so that 1.5% water solution of No. 3 silicate of soda might be kept at 70 degrees C and the contact time of an aluminum web might become 15 seconds, and it was rinsed further. The coating weight of Si was 10 mg/m<sup>2</sup>. This substrate is set to [AS-2].

[0115] the procedure of [painting of interlayer] following -- SG -- the liquefied constituent (sol liquid) of law was adjusted. Weighing capacity of the following constituent was carried out to the beaker, and it stirred for 20 minutes at 25 degrees C.

A tetra-ethoxy silane 38g 3-methacryloxy propyl trimethoxysilane 13g 85% phosphoric-acid water solution 12g Ion exchange water 15g Methanol 100g [0116] This solution was moved to the three necked flask, the reflux condenser was attached, and the three necked flask was dipped in the oil bath of a room temperature. It was made to go up to 50 degrees C in 30 minutes, stirring the contents of a three necked flask with a magnetic stirrer. Keeping bath temperature at 50 degrees C, it was made to react for further 1 hour, and the liquid constituent (sol liquid) was obtained. It diluted so that a methanol / ethylene glycol =20 / 1 (weight ratio) might make 0.5% of the weight, and whirler spreading was carried out at said aluminum substrate [AS-1], and this sol liquid was dried at 100 degrees C for 1 minute. The coverage at that time was 3.5 mg/m<sup>2</sup>. This coverage calculated the amount of Si elements by the cay light X-ray analysis, and made it coverage. Thus, the created base material is set to [AS-3]. Next, the liquid of the following presentation was applied to the aluminum base material [AS-2] with the wire bar, and it dried for 30 seconds at 90 degrees C using the warm air type dryer. The amount of clothing after

desiccation was 10 mg/m<sup>2</sup>.

[0117]

Ethyl methacrylate and 2-acrylamide-2-methyl-1-Copolymer of the mole ratio 75:15 of propane sulfonic-acid sodium salt 0.1g 2-aminoethylphosphonic acid 0.1g Methanol 50g Ion exchange water The base material created in this way 50g is set to [AS-4].

[0118] Applied the negative-mold photosensitivity constituent of the following presentation so that desiccation coverage might turn into an amount given in Table 2, and it was made to dry for 1 minute at 100 degrees C, and the sensitization layer was made to form on [painting of a sensitization layer], thus the processed aluminum plate.

[0119]

(Negative-mold photosensitivity constituent)

An addition polymerization nature compound (compound of a publication all over Table.2) 1.5g Binder polymer (compound of a publication all over Table 1) 2.0g Sensitizing dye (compound of a publication all over Table 2) 0.2g Photopolymerization initiator (compound of a publication all over Table 2) 0.4g \*\* -- sensitizing dye (compound of a publication all over Table 2) 0.4g Fluorine system nonionic surface active agent 0.03g (the Dainippon Ink & Chemicals, Inc. make, megger fuck F-177)

Thermal polymerization inhibitor 0.01g (aluminium N-nitrosophenyl-hydroxylamine)

Color pigment distribution object of the following presentation 2.0g Methyl ethyl ketone 20.0g

Propylene glycol monomethyl ether 20.0g [0120]

(Color pigment distribution object presentation)

Pigment Blue 15:6 15 weight sections Allyl compound methacrylate / methacrylic-acid copolymer Ten weight sections (copolymerization mole ratios 80/20, weight average molecular weight 40,000)

Cyclohexanone 15 weight sections Methoxy propyl acetate 20 weight sections Propylene glycol monomethyl ether 40 weight sections [0121] [painting of a protective layer] -- on this sensitization layer, 3% of the weight of the water solution of polyvinyl alcohol (whenever [ saponification ] 98-mol %, polymerization degree 550) was applied so that desiccation spreading weight might serve as 2 g/m<sup>2</sup>, and it dried for 2 minutes at 100 degrees C.

[0122] A FD-YAG (532nm) laser exposure machine (Hy Dell Berg plate setter: Gout Teng Berg) is used for the negative-mold photosensitivity monotonous printing version which is [exposure of negative-mold photosensitivity monotonous printing version] above, and was made and obtained. Exposure power was adjusted so that it might become printing plate exposure energy-density J/cm<sup>2</sup> of 200micro, and solid image exposure and 2540dpi, 175 lines / inch, and halftone dot image exposure that becomes 1 to 99% by unit 1% were performed.

[0123] [development/platemaking] Fuji Photo Film Co., Ltd. make -- auto-processor FLP-813 -- a developer given in Table 3, and the Fuji Photo Film Co., Ltd. make -- finisher FP-2W were taught, respectively, the version [ finishing / exposure ] was developed / engraved on the developer temperature of 30 degrees C, and the conditions for developing time 18 seconds, and the lithography version was obtained.

[0124] Made in [ R201 ] Roland was used as a [image section print resistance test] printing machine, and Dainippon Ink graph G (N) was used as ink. The printed matter of the solid image section was observed and the number of sheets in which an image began to become blurred investigated image section print durability. Print durability is so good that a figure is large.

[0125] Made in [ R201 ] Roland was used as a [halftone dot print durability forcible trial] printing machine, and Dainippon Ink graph G (N) was used as ink. the 5,000th sheet from printing initiation -- the Fuji Photo Film Co., Ltd. make -- PS plate cleaner CL-2 were infiltrated into the sponge for printing, the halftone dot section was wiped, and the ink of a printing plate was washed. Then, 10,000-sheet printing was performed and the existence of a version jump of the halftone dot in printed matter was observed visually.

[0126] (Examples 21-30, examples 4-6 of a comparison) The engine performance was evaluated about the negative-mold photosensitivity monotonous printing version shown in Table 4 like examples 1-20.

[0127] Below, each compound indicated in Table 3 and 4 is shown.

[Addition polymerization nature compound]

M-1: Pen TAERUSURI toll tetraacrylate (Shin-Nakamura Chemical Co., Ltd. make; NK ester A-TMMT)

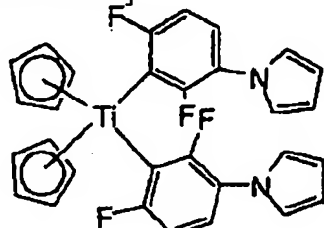
M-2: Glycerol dimethacrylate hexamethylene di-isocyanate urethane prepolymer (the product made from Kyoeisha Chemistry; UA101H)

M-3: Dipentaerythritol acrylate (Shin-Nakamura Chemical Co., Ltd. make; NK ester A-9530)

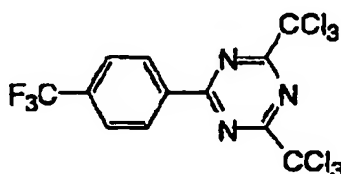
[The material for photopolymerization initiators in Tables 3 and 4]

[0128]

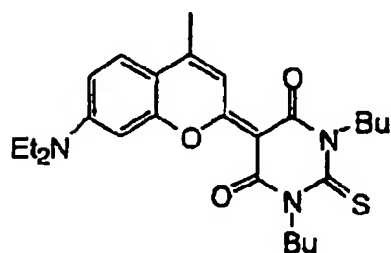
[Formula 17]



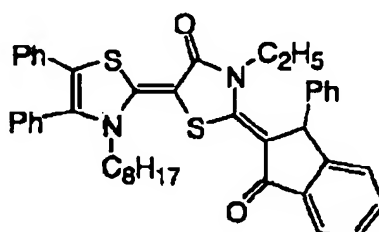
I-1



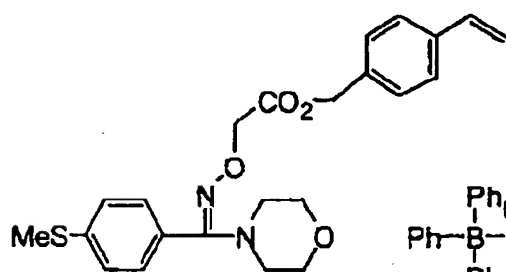
I-2



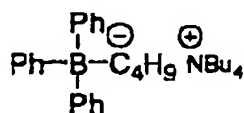
S-1



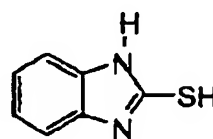
S-2



C-1



C-2



C-3

[0129] [Binder polymer]

A PR-1 methacrylic-acid allyl compound (POC-1) / methacrylic-acid copolymer (copolymerization mole ratio; 80/20)

The weight-average-molecular-weight 48,000--2 methacrylic-acid allyl compound (POC-1) / 2-[2-(methacryloyloxy) ethoxycarbonyl] benzoic-acid copolymer for which it asked from the observation acid-number 1.70 meq/gGPC measurement for which it asked with NaOH titration (copolymerization mole ratio; 70/30)

The weight-average-molecular-weight 95,000--3 methacrylic-acid allyl compound / 3-[2-(methacryloyloxy) ethoxycarbonyl] propionic-acid copolymer for which it asked from the observation acid-number 1.72 meq/gGPC measurement for which it asked with NaOH titration (copolymerization mole ratio; 70/30)

The weight-average-molecular-weight 95,000PA-1 following diisocyanate for which it asked from the observation acid-number 1.72 meq/gGPC measurement for which it asked with NaOH titration, and polyurethane resin 4, 4'-diphenylmethane IIISOISOSHINETO (MDI) which are the condensation polymerization object of diol

Hexamethylene di-isocyanate (HMDI)

A polypropylene gowy recall, weight average molecular weight 1000 (PPG1000)

2 and 2-bis(hydroxymethyl) propionic acid (DMPA)

The weight-average-molecular-weight 45,000PA-2 methyl methacrylate / acrylonitrile / N-[(4-sulfamoyl) phenyl] methacrylamide copolymer for which it asked from the observation acid-number 1.05 meq/gGPC measurement for which it asked with copolymerization mole ratio

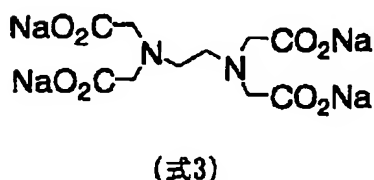
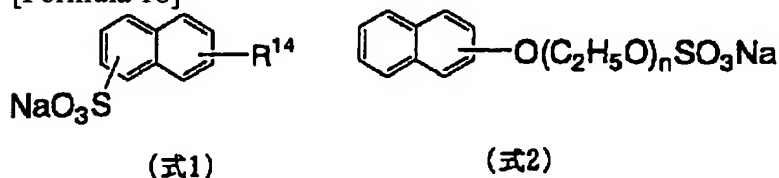
(MDI/HMDI/PPG1000/DMPA) 40 / 10/15 / 35NaOH titration (copolymerization mole ratio; 37/30/33)

Weight-average-molecular-weight 49,000 for which it asked from GPC measurement [0130]

[Developer]

Water-solution monoethanolamine of pH10 which consists of the D-1 following presentation 0.1 Weight section triethanolamine 1.5 Compound of the weight section following type 1 4.0 Compound of the weight section following type 2 2.5 Compound of the weight section following type 3 0.2 Weight \*\*\*\* 91.7 Weight section [0131]

[Formula 18]



[0132] R14 expresses a hydrogen atom or butyl during the above (formula 1).

Water-solution 1K potassium silicate which consists of the D-2 following presentation 3.0 Weight section potassium hydroxide 1.5 Compound of the weight section aforementioned type 3 0.2 Weight \*\*\*\* 95.3 Weight section [0133]

[Table 3]



表 3

No.	支持体	感光層						現像液	耐刷性	
		付加重合性化合物	バインダーポリマー	光重合開始剤	増感色素	共増感剤	乾燥塗布量 (g/m <sup>2</sup> )		画像部 (万枚)	網点部
実施例 1	AS-3	M-1	P-1	I-1	S-1	C-1	1.4	D-2	40	極めて良好
実施例 2	AS-3	M-1	P-2	I-1	S-2	C-1	1.3	D-2	22	良好
実施例 3	AS-3	M-2	P-4	I-2	S-1	C-1	1.4	D-2	33	極めて良好
実施例 4	AS-1	M-2	P-5	I-1	S-2	C-1	1.4	D-1	35	良好
実施例 5	AS-3	M-2	P-7	I-1	S-2	C-2	1.4	D-2	33	良好
実施例 6	AS-3	M-3	P-9	I-2	S-1	C-3	1.6	D-2	27	極めて良好
実施例 7	AS-3	M-1	P-11	I-1	S-1	C-1	1.2	D-2	28	良好
実施例 8	AS-3	M-1	P-13	I-1	S-2	C-1	1.4	D-1	37	極めて良好
実施例 9	AS-1	M-2	P-16	I-2	S-1	C-1	1.4	D-2	37	極めて良好
実施例 10	AS-1	M-2	P-17	I-2	S-1	C-2	1.5	D-1	34	極めて良好
実施例 11	AS-3	M-2	P-18	I-1	S-1	C-2	1.4	D-2	21	良好
実施例 12	AS-3	M-2	P-20	I-1	S-2	C-1	1.3	D-2	27	極めて良好
実施例 13	AS-1	M-3	P-22	I-2	S-1	C-1	1.4	D-2	25	極めて良好
実施例 14	AS-3	M-3	P-23	I-1	S-2	C-3	1.7	D-1	23	極めて良好
実施例 15	AS-3	M-1	P-24	I-2	S-1	C-1	1.4	D-2	27	良好
実施例 16	AS-3	M-2	P-25	I-1	S-2	C-1	1.3	D-2	27	極めて良好
実施例 17	AS-1	M-3	P-26	I-2	S-1	C-1	1.4	D-2	25	良好
実施例 18	AS-3	M-3	P-27	I-1	S-2	C-3	1.7	D-1	23	極めて良好
実施例 19	AS-1	M-2	P-28	I-1	S-2	C-3	1.5	D-1	30	良好
実施例 20	AS-3	M-1	P-29	I-2	S-1	C-1	1.4	D-2	27	良好
比較例 1	AS-3	M-1	PR-1	I-1	S-1	C-1	1.4	D-2	5	極めて良好
比較例 2	AS-3	M-1	PR-2	I-2	S-2	C-1	1.4	D-2	11	版飛び
比較例 3	AS-3	M-2	PR-3	I-1	S-1	C-2	1.4	D-2	4	版飛び

[0134]

[Table 4]

表 4

No.	支持体	感光層										耐刷性	
		付加重合性 化合物	バインダーポリマー		重量比 (1:2)	光重合 開始剤	増感色素	共増感剤	乾燥塗布量 (g/m <sup>2</sup> )	現像液	画像部 (万枚)	網点部	
			1	2									
実施例21	AS-1	M-1	P-3	P-6	5/5	I-1	S-2	C-1	1.4	D-2	30	良好	
実施例22	AS-3	M-3	P-8	P-21	6/4	I-1	S-1	C-1	1.2	D-2	28	良好	
実施例23	AS-3	M-2	P-8	P-30	7/3	I-2	S-1	C-2	1.2	D-2	34	良好	
実施例24	AS-1	M-2	P-10	P-21	8/2	I-1	S-1	C-1	1.4	D-1	33	良好	
実施例25	AS-3	M-1	P-12	P-28	9/1	I-2	S-2	C-3	1.4	D-1	21	極めて良好	
実施例26	AS-3	M-1	P-14	P-15	3/7	I-2	S-1	C-1	1.6	D-2	24	極めて良好	
実施例27	AS-1	M-2	P-1	PA-1	8/2	I-1	S-1	C-1	1.4	D-2	21	極めて良好	
実施例28	AS-3	M-3	P-10	PA-2	5/5	I-1	S-1	C-1	1.4	D-1	23	極めて良好	
実施例29	AS-3	M-2	P-10	PA-2	7/3	I-2	S-2	C-3	1.7	D-1	22	極めて良好	
実施例30	AS-3	M-1	P-26	PR-3	7/3	I-2	S-2	C-1	1.2	D-1	27	良好	
比較例4	AS-3	M-2	P-1	PA-1	5/5	I-2	S-2	C-1	1.3	D-2	9	版飛び	
比較例5	AS-1	M-2	P-1	PA-2	8/2	I-1	S-1	C-1	1.5	D-2	4	良好	
比較例6	AS-3	M-3	P-3	PA-1	9/1	I-1	S-1	C-3	1.5	D-1	20	版飛び	

[0135] (Examples 31-50, examples 7-9 of a comparison)

The [painting of sensitization layer] following sensitization layer coating liquid was adjusted, it applied so that a wire bar might be used for an aluminum base material [AS-4] and the amount of covering after desiccation might turn into an amount given in Table 5, and it dried for 45 seconds at 115 degrees C

with the warm air type dryer, and the sensitization layer was formed.

[0136]

Sensitization layer coating liquid Addition polymerization nature compound (compound of a publication all over Table 2) 1.0g Binder polymer (compound of a publication all over Table 5) 1.0g Infrared absorption agent (IR-1) 0.08g Thermal polymerization initiator (compound of a publication all over Table 5) 0.3g Fluorine system nonionic surface active agent 0.01g (the Dainippon Ink & Chemicals, Inc. make, megger fuck F-176)

Naphthalene sulfonate of Victoria pure blue 0.04g Methyl ethyl ketone 9.0g Propylene glycol monomethyl ether 8.0g Methanol 10.0g [0137] [painting of a protective layer] -- it applied so that desiccation spreading weight might serve as 2 g/m<sup>2</sup> if needed in 3% of the weight of the water solution of polyvinyl alcohol (whenever [ saponification ] 98-mol %, polymerization degree 550) on this sensitization layer, and it dried for 2 minutes at 100 degrees C.

[0138] [exposure of the negative-mold photosensitivity monotonous printing version] -- the negative-mold photosensitivity monotonous printing version obtained as mentioned above was exposed on condition that output 9W, outside drum rotational frequency 210rpm, printing plate energy 100 mJ/cm<sup>2</sup>, and resolution 2400dpi in Trendsetter3244VFS made from Creo which carried water cooling type 40W infrared semiconductor laser.

[0139] auto-processor SUTABURON after [ [development/platemaking] exposure ] and by Fuji Photo Film Co., Ltd. 900N -- a developer given in Table 5, and finisher Fuji Photo Film Co., Ltd. make -- the 1:1 water diluent development of FN-6 was taught, respectively, it developed negatives/engraved at 30 degrees C, and the lithography version was obtained.

[0140] RISURON by KOMORI CORP. was used as a [image section print resistance test] printing machine, and Dainippon Ink graph G (N) was used as ink. The printed matter of the solid image section was observed and the number of sheets in which an image began to become blurred investigated image section print durability. Print durability is so good that a figure is large.

[0141] RISURON by KOMORI CORP. was used as a [halftone dot print durability forcible trial] printing machine, and Dainippon Ink graph G (N) was used as ink. the 5,000th sheet from printing initiation -- the Fuji Photo Film Co., Ltd. make -- PS plate cleaner CL-2 were infiltrated into the sponge for printing, the halftone dot section was wiped, and the ink of a printing plate was washed. Then, 10,000-sheet printing was performed and the existence of a version jump of the halftone dot in printed matter was observed visually.

[0142]

[Table 5]

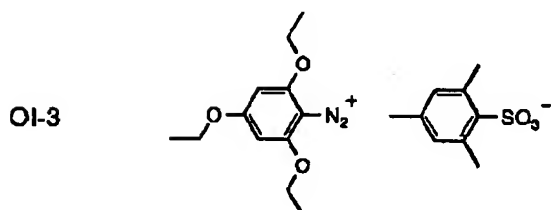
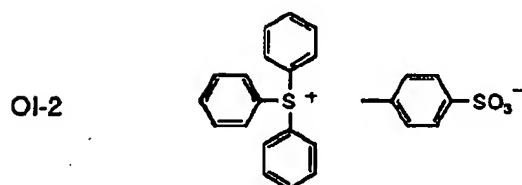
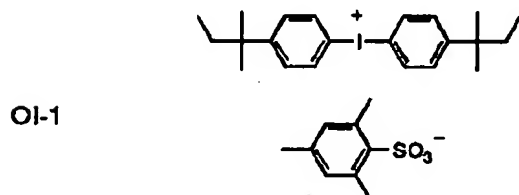
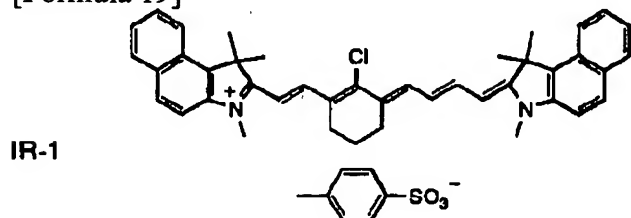
表 5

No.	支持体	感光層							保護層	現像液	耐刮性	
		付加重合性 化合物	バインダーポリマー		重量比 (1:2)	熱重合 開始剤	乾燥塗布量 (g/m <sup>2</sup> )	画像部 (万枚)			網点部	
			1	2								
実施例 31	AS-4	M-3	P-2	なし	-	OI-1	1.4	なし	D-3	38	極めて良好	
実施例 22	AS-4	M-3	P-3	なし	-	OI-1	1.2	あり	D-3	40	良好	
実施例 33	AS-1	M-2	P-5	なし	-	OI-2	1.2	なし	D-2	25	良好	
実施例 34	AS-4	M-1	P-7	なし	-	OI-1	1.2	あり	D-1	33	極めて良好	
実施例 35	AS-2	M-3	P-11	なし	-	OI-2	1.3	なし	D-3	21	極めて良好	
実施例 36	AS-4	M-3	P-14	なし	-	OI-3	1.1	なし	D-3	28	極めて良好	
実施例 37	AS-3	M-2	P-16	なし	-	OI-1	1.3	あり	D-3	32	極めて良好	
実施例 38	AS-3	M-2	P-19	なし	-	OI-1	1.3	なし	D-2	23	極めて良好	
実施例 39	AS-4	M-1	P-21	なし	-	OI-2	1.3	なし	D-1	36	極めて良好	
実施例 40	AS-4	M-1	P-23	なし	-	OI-2	1.5	あり	D-1	27	良好	
実施例 41	AS-3	M-3	P-25	なし	-	OI-3	1.2	あり	D-3	30	良好	
実施例 42	AS-3	M-3	P-27	なし	-	OI-1	1.3	なし	D-2	24	良好	
実施例 43	AS-4	M-3	P-29	なし	-	OI-2	1.4	なし	D-1	34	良好	
実施例 44	AS-4	M-2	P-10	P-6	8/2	OI-1	1.2	あり	D-3	33	良好	
実施例 45	AS-2	M-1	P-12	P-24	9/1	OI-3	1.2	なし	D-3	21	極めて良好	
実施例 46	AS-4	M-3	P-14	PR-1	8/2	OI-2	1.3	なし	D-2	24	極めて良好	
実施例 47	AS-4	M-2	P-1	PA-1	8/2	OI-2	1.3	なし	D-1	36	極めて良好	
実施例 48	AS-3	M-3	P-10	PA-2	5/5	OI-1	1.4	あり	D-3	23	極めて良好	
実施例 49	AS-3	M-2	P-10	PA-2	7/3	OI-1	1.1	なし	D-3	22	極めて良好	
実施例 50	AS-1	M-3	P-26	PR-3	7/3	OI-2	1.3	なし	D-1	27	良好	
比較例 7	AS-4	M-3	P-1	なし	-	OI-1	1.3	なし	D-1	3	版飛び	
比較例 8	AS-4	M-2	P-2	なし	-	OI-1	1.2	なし	D-3	5	良好	
比較例 9	AS-4	M-3	P-3	PA-1	9/1	OI-3	1.2	あり	D-3	10	版飛び	

[0143] [The thermal polymerization initiator in Table 5]

[0144]

[Formula 19]



[0145]

[The developer in Table 5]

D-3 The monohydrate of a sodium carbonate 10g Potassium hydrogencarbonate 10g Isopropyl naphthalene sulfonic-acid sodium 15g Dibutyl naphthalene sulfonic-acid sodium 15g Ethylene glycol MONONAFUCHIRUETERU mono-sulfate Sodium salt 10g Sodium sulfite 1g

Ethylenediaminetetraacetic acid 4 sodium 0.1g Ion exchange water 938.9g [0146] The printing version which was very excellent and which \*\*\*\*\* was obtained from the negative-mold photosensitivity monotonous printing version which prepared the sensitization layer containing the giant-molecule binder which has the repeat structure expressed with a general formula (I) so that clearly from Tables 3-5.

[0147]

[Effect of the Invention] As explained above, the negative-mold photosensitivity monotonous printing version of this invention gives the lithography version which has very high print durability by preparing the sensitization layer containing the giant-molecule binder which has the repeat structure expressed with a general formula (I). Moreover, the negative-mold photosensitivity monotonous printing version of this invention fits the scan exposure by the laser beam, and the writing in a high speed is possible for it, and it has high productivity.

[Translation done.]